INTERNAL ENERGY

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A METHOD PROPOSED FOR THE CALCULATION OF ENERGY STORED WITHIN MATTER.

INTRODUCTION.

The purpose of this paper is to suggest a simple working hypothesis whereby the amount of chemical energy stored within a body may be estimated. The work is based upon various lines of experimental data and here only a general outline will be sketched, the paper itself giving all details.

The idea originated several years ago from a mathematical study of the periodic curves of the atomic volumes and melting-points. Through a combination of the methods of algebra and analytical geometry the attempt was made to discover why these curves were not solvable through the values of their ordinates.

Two results followed. It was ascertained in the first place that to accomplish this purpose the determination of several constants was necessary and secondly that, as heat measured chemical energy, possibly chemical change could be measured by expansion through heat.

A mathematical method was devised for expressing the relations of heat to mass through great ranges of temperature.

By this means it was believed errors of observation could be minimized. Eventually several constants were disclosed.

Heat was recognized as a common agent, producing expansion in all bodies and developing great force in each unit volume.

Hence, if the conditions of physical change could be measured in any one system the same method must apply to all others.

The method as devised was first applied to two elements iron and copper, though it was recognized that merchantable materials were rather alloys than pure elements. Later, the method was applied to a manufactured alloy known in trade as Muntzmetal.

The results were strikingly similar, especially when conditions of expansion for the gaseous state were reached.

They evidently tended towards an expression of a constant gaseous coefficient of expansion at a rate of 1/273 per degree.

This hypothesis was adopted and a new study entered into to ascertain what changes were necessary to cover similar relations in any material.

This constant degree of physical change was the basis naturally chosen. Here the rate of change of mass to volume was specific and a number of constants were determined.

In order to test the accuracy of the method, mathematical means were employed to change certain equations given in the paper. As stated, these equations are based upon the idea that all physical change can be measured by heat, and that all matter reaches a common measure in the gaseous condition.

The change consists in deriving an equation expressing the conditions to be found in copper from one based upon similar conditions found in iron through the use of certain constants.

By this means it was found that both sets of experimental data, those expressing the relations of heat to mass for iron and for copper, were calculable from the same equation.

By corresponding changes, those for Muntz-metal were calculated from the same data.

Finally, similar results were obtained from six metals at considerable ranges of temperature. These included zinc, tin, bismuth and lead.

An attempt was made to estimate the amounts of energy due to physical change between certain fixed stations or temperatures. The idea of fixed amounts of expansion measuring fixed periods of change per unit mass was brought to bear and a method devised to determine the strain of volume met with during the interval. Then the energy developed was to be measured by the product of the average stress into this strain of volume.

In this manner it was sought to measure the latent heats of vaporization.

Determinations were attempted for ten individual cases and the results compared with experimental values. Some of these results fall above and others below the latter.

For instance, Water figures	105.1%	of the experimental	
Bromine "	97.13	"	"
Benzene "	96.37	"	"
$C\,S_2$ "	93.28	"	"

The general average of the ten determinations is 98.4%.

By an examination of the geometrical constant defining the equality of the gaseous expansion at the rate of 1/273 per degree and by calculations of the energy developed through well defined periods thereby described, we arrive at two values of energy rates. These values practically correspond to 5.2 and 6.7 known as the atomic heats.

Judging from the factors determining these rates and from their development in relation to each other, they must represent the development of energy of two distinct physical conditions, which this paper seeks to explain, hypothetically.

The difference between the rates of energy gained by expansion in a fixed interval must represent the latent heat of fusion. This interval can be accurately defined.

Among the values are:

	Calculated values	Experimental values.
Zn	23.34 cals.	28.1 cals.
Ga	24.9 "	19.11 "
Br	19.05 "	16.18 "
Cd	13.60 "	13.66 "
Sn	12.79 "	14.25 "
I	12.01 "	11.7 "
Water	84.6 "	80.02 "

If we turn now to a study of Thomsen's experiments in solution and dilution, we find his results are to a great extent summed under empirical formulæ.

When these are examined under our methods the relation of the constants he has determined can be readily interpreted from their resemblance to ours.

The latter describe the energy of some degree or rate of change. Hence a new reading can be given to these formulæ.

The law they express can be written in words, instead of in figures.

The various results to which we have thus far referred are mainly physical in their development, though the last lie just on the border line of chemistry.

In the paper a few other comparisons of experimental and calculated results are added to the above.

Eventually, however, the study turns to the development of chemical energy and its measure.

In the calculation of the chemical energy a method is suggested for estimating the number of calories freed by the change of 96 grams of ozone to oxygen.

The experimental result is 68,000, the calculated one 69,880.

Attention is then turned to methods of calculating Heats of Formation.

The following are examples of some of the results obtained:

Substances.	Calculated Values, cals.	Experimental Values, cals.
H_2S	4833.7	4740.
ICl	5937.	5830.
PbI_2	39195.	39800.
$CdCl_2$	92995.	93244.
$HgCl_2$	63507.	63160.
$CdBr_2$	75057.	75200.
H_2O	68321.	68360.

Thus a general outline of the suggested methods for the calculation of the amounts of energy stored in matter is presented.

While other data are at hand, it is believed that sufficient have been given to enable the reader to judge of their merit.

The thanks of the writer are due to Dr. Jos. A. Deghuée for careful and valuable criticism upon the contents of this paper.

The writer feels that each reader of these pages will regard them with a different amount of skepticism, for each one will naturally be guided by his personal experiences.

Hence he fears that the results to be attained can only be of variable character for the present. He trusts, however, that eventually the paper may meet with the approval of some who will give it earnest attention, for it can only be accepted through the efforts of this latter class.

EXPANSION A MEASURE OF PHYSICAL CHANGE.

Expansion has been universally recognized as a measure of the increasing distance between molecules, the increase of volume being a function of the amount of energy imparted and stored during the specific change of temperature and the cohesion of the mass being rapidly reduced by the increasing distance.

In the practical measure of expansion in materials under physical change all experimental results indicate the existence of a general law, but owing to the imperfection of the conditions of the specimen in its natural state, an accurate expression of this law is seldom arrived at.

It is generally recognized that the linear expansion of a solid is expressed by $1' = 1'' \, (1 + a\,t)$, when t represents the change in temperature and a the linear expansion coefficient.

The volumetric expansion can be expressed as

$$V' = V'' \, (1 + a\,t)^3$$

or by an equation of the third degree, indicating a growth in the three axial directions.

At the same time we must understand that while this equation expresses the natural law governing the change, matter owing to its porous condition cannot always expand outwardly as if it were solid. Hence practical experience often indicates the true law only through an approximation.

COHESION VS. HEAT.

In an examination of this subject our attention is at once called to variations in the recorded values of the melting-points, both among the elements and among the composite bodies. In fact it is seldom, if ever, that any two records agree exactly.

This variation is greatest among the alloys and we can realize how the presence of a very small percentage of foreign matter would produce such a result.

This is most readily appreciated in the case of commercial

irons and coppers. In the former, where the element is never found pure, slight changes in composition alter the material from cast to wrought iron, or to steel, while the internal conditions vary greatly, as shown by the reigning cohesive stresses. Among the latter class of metals similar variations are found, resulting from admixtures of silver, lead, potassa, etc.

The melting-points of irons vary from 1100° to 1800° C, while those of commercial coppers range from 1080° to 1398° C.

This is of little importance to us in our present research, for the laws of cohesion being universal must hold good, whether other ingredients are present or not.

It is then immaterial to us whether, in the search for the general law, we examine the cohesion of iron or steel, of copper or of some alloy of these metals.

In every case the struggle of " Cohesion vs. Heat " must be expressed by the changes occurring within the material with rising temperature. They determine the rate of expansion of the body.

In order to present a more definite idea of this struggle, it will be well to sketch a theoretical view of the situation.

We must suppose each individual kind of matter, elementary or composite, to be possessed of its own amount of cohesion at our initial station, the absolute zero of temperature.

With compact specimens this amount will be greater than with porous ones of the same character, as the density will be greater.

Each of these when subjected to heat will gradually lose its cohesion and will finally become fluid.

As already stated, chemical change by admixture of other bodies affects the cohesion of the mass and thus incidentally the melting-points.

This latter station may also be changed by physical means for instance, by rolling or wiredrawing, by which the particles are crowded together and cohesion increased.

When certain kinds of material are exposed to high temperatures, their internal conditions may be altered by the methods used in cooling to normal temperatures. Various amounts of the energy thus offered may be retained by them and utilized in physical change in various degrees.

In many cases when protected against a loss of heat, being

forced to cool slowly and evenly through their mass, their internal stresses are weakened. The metal is then annealed.

Again, when their external surfaces are suddenly cooled, by dipping or quenching in cool liquids, the metal is tempered.

Then the internal stresses are greatly increased and the metal hardened.

By these means greater or lesser amounts of cohesion may be added or deducted from that previously held by the mass.

But in any case, with these changes to their systems, and with a struggle originating from absolute zero, it is clear that each individual kind of matter must have its own internal struggle, one determined by its own store of cohesion.

It becomes of prime importance then to get some reliable expression of the relations existing between these forces, our agents, in binding and freeing the internal parts of some material. As the struggle is omnipresent a general law governing physical change must exist into which it will be well to examine. For an accurate basis of examination we are naturally driven to experimental results, giving a preference to determinations having the longest range of temperature.

Several series of tests exist, made with great care, where similar specimens of materials have been submitted to rupture tests at various temperatures, some of the latter approaching well towards the melting-point.

A number of such results are shown on Charts 1 and 2. The former records the results obtained from various grades of iron and steel, the latter those of copper.

On these charts the absolute temperature of the experiment is shown on the abscissa, while the rupture test, representing the balance of cohesion left at that point, forms the ordinate.

The charts thus show the actual change in cohesion as the molecules are moved to greater distances apart.

Great differences are recorded between the acting stresses of the various grades of material at common temperatures, though we know the individual changes in the unit mass to be very small.

Apparently then we are justified in concluding that each independent curve is a record of an individual struggle, a representative of one specific alloy differing from its neighbors at every point of change, even including its melting-point.

For it is evident from the various values of cohesive stress at the last station 1100° C that each curve will find its own zero on the abscissa, or its own melting-point, thus confirming the general and previous experimental evidence.

It is evident that with changes of crystallization due either to wiredrawing or to changes of temper, we may increase or decrease the natural store of energy of a body, as we may also do by a chemical change. The charges of cohesion can then

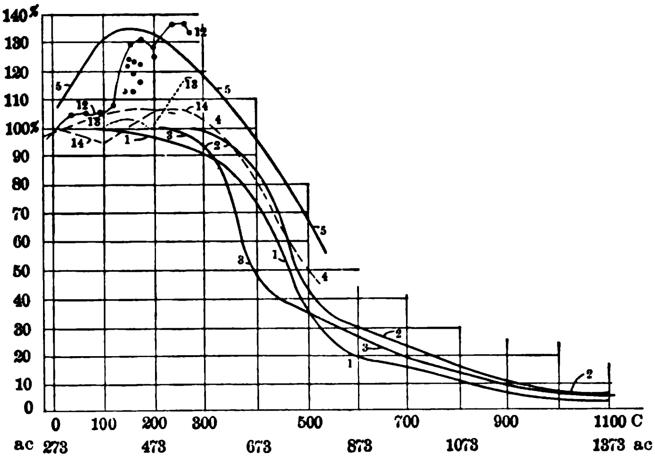


CHART 1.—Irons and Steels.

NOTE.—Curves Nos. 1 and 2 Kohlman's Iron; 3 Kohlman's Steel; 4 Franklin Institute: 5 Fairbairn's English Irons; 12 and 13 British Admiralty Irons; 14 Siemen's Steel. Dots show some of Styffe's results. The diagram exhibits the general accordance of later investigations with that of the Franklin Institute of 1835. (Thurston.)

increase or decrease so that each individual may have its natural charge plus or minus these accidental charges.

The actual results given in the charts prove that each variety or class of bodies has individual characteristics dependent upon the nature of the ingredients bound in the finished specimen after the usual treatment changing the original ore into a merchantable product.

Many of the ingredients are left intentionally, or are added in specific amounts for the purpose of augmenting or of de-

creasing the degree of tenacity, ductility or hardness inherent in the material.

Now, while it is acknowledged that all these changes do occur in materials, we must bear in mind that rupture tests are generally adopted by experts when a reliable expression of these attributes of a material, in any of its grades, is desired.

Many manufacturers guarantee to deliver large amounts of articles under specific grades in these very properties, whether of high or of low degree, any piece so delivered being subject to this rupture test.

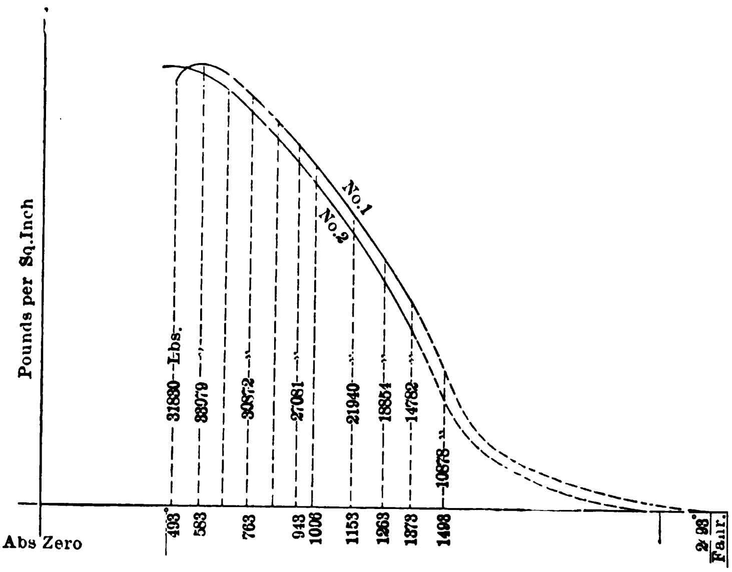


CHART 2.—Strength of Copper from the Franklin Institute.
Note.—Curve No. 1 line of 1837; No. 2 from Nystrom.

Thus a specified ductility under a fixed rupture test is recognized as a scientific means of distinguishing the desired grade of material, it being under control during the process of manufacture.

If then this rupture test can detect variations in ductility as well as in tenacity, why should it not be a suitable agent to employ in a study of other attributes of matter?

As shown these tests apparently indicate that each grade has its own melting-point, and we know it has its own specific gravity.

Hence the determination to apply these tests to a study of the variations of cohesion by expansion.

There is perhaps one other peculiarity to be noted upon Chart 1 that can be mentioned.

Certain experiments by Styffe* upon Swedish irons and steels, with high carbon, yield a number of results that are indicated by dots upon the chart, and are located between the curves 12 and 13, at low temperatures.

In this field the results obtained from similar specimens are so discordant that apparently they cannot be joined upon a consecutive curve. To a certain extent this irregularity is still shown in the adjacent curves 12 and 13.

The latter are still quite irregular but, as shown, determine curves possessing sudden changes that even repeat themselves under various increases and decreases in cohesive stress.

At present it is sought only to call attention to this fact with the intention of recurring to it later.

Returning to the main question it can be noted that, in addition to the data shown in our charts, other well known results may be quoted to show that each material must have its own curve.

The familiar instance of the cold short and the red short irons may be mentioned. It is also known that these conditions are due to the foreign ingredients held, and that certain quantities of potassa and of sulphur produce these changes.

It is very evident that under such conditions the charts must have strong individual characters.

As regards the accuracy of the charts as a record of tests, it is evident that they must be fully up to the average, when compared with those of most physical and chemical experiments; for, with stresses in steel decreasing from 100,000 lbs. per square inch to zero, and in wrought iron from 36,000 lbs. to zero, and with temperatures at the same time increasing from laboratory temperature to 1100° C. we have enormous ranges.

They are equaled in few cases, and it is very evident that the error of a few degrees in observation will have little influence upon the result.

The laws governing this struggle therefore must be expressed

*Thurston's "Materials," page 491.

closely in each and every curve. Each line must embody the individual characteristics of its specimen. Its expansion varies with its composition, but the cohesion dependent upon such expansion must always be measured by the heat applied in raising the temperature from a point of origin where the motion of heat originates to that point where cohesion equals zero the melting-point.

THE FORMULA.

Having thus considered these rupture tests in a general way, it is desired to adapt, for our purposes, a particular series that have been taken from Nystrom's Mechanics, the author stating that they are from experiments made by the Franklin Institute.

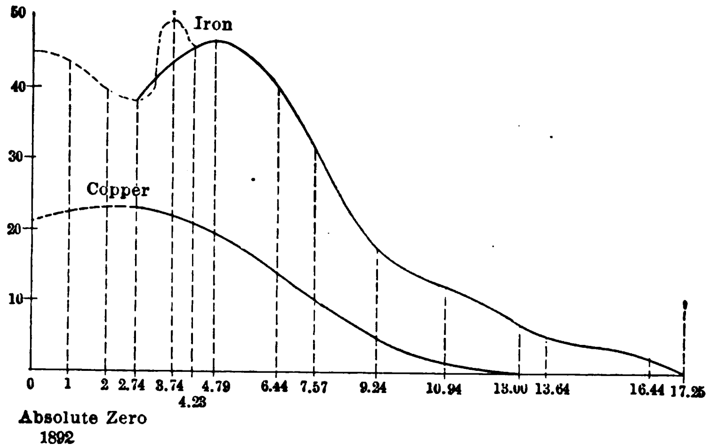


CHART A.—Cohesion vs. Heat.
Note.—Compare with Thurston Materials, page 491, No. 12.

These data are shown in Tables I and II.

Chart A also is presented showing the curves in full lines.

There are two sets of experimental results, one made upon iron and one upon copper specimens at various temperatures.

Column 1, in each table, gives the temperatures at which the ruptures occurred, while column 2 gives the respective breaking stresses in pounds per square inch.

For our present purposes these values are changes to other denominations. Column 3 shows the rupture tests reduced to

kilograms per square millimeter. Column 4 gives the temperatures in absolute centigrade degrees divided by one hundred, or $\frac{\text{a.c.*}}{100}$.

On Chart A the temperatures $\frac{\text{a.c.}}{100}$ are recorded along the abscissa representing values of X, while the rupture tests, as given in Column 3, are shown as ordinates, or as values of Y.

COPPER, TABLE I.

T.° C	lbs. sq. in.	Kilo sq, mm.	$\frac{t}{100}$ a, c.
1	2	3 Y	4 X
0.	32800	23.0584	2.74
149.	29500	20.7385	4.23
205.	27400	19.2622	4.79
260.	25300	17.7859	5.34
370.	20100	14.1303	6.44
427.	17200	12.0916	7.01
483.	14000	9.842	7.57
1026.		0.	13. †
93.3	31000	21.7936	3.673
		Y	X

But these relative values of X and Y, as pairs of coördinates, have a mathematical significance deeper than that shown to the eye on the chart.

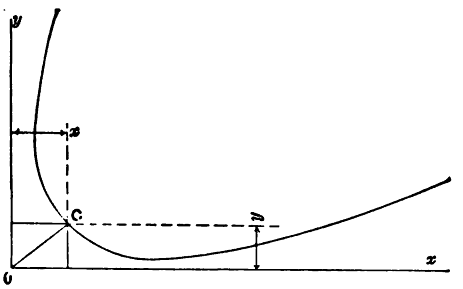
In any coördinate system, each set of experimental data locates a point of intersection, on the plan, as at C and the line $O\,C$ drawn from O as a point of origin indicates in direction and magnitude the resultant of X and Y. The geometrical

* When these calculations were made 274 was added to the experimental value instead of 273.

†With the intention of extending the line of temperatures of observation the melting-point of copper at 1300° C. was added to the experimental tests in Table I.

IRON, TABLE II.

T.° C.	lbs. sq. in.	Kilo sq. mm.	$\frac{t}{100}$ a, c.
1	2	3 Y	4 X
0.	55000	38.665	2.74
149.	65750	46.222	4.23
205.	67000	47.01	4.79
370.	57800	40.633	6.44
483.	45000	31.635	7.57
650.	25000	17.575	9.24
820.	16500	11.60	10.95
1090.	7000	4.921	13.64
1370.	2500	1.7575	16.44
		Y	X



position thus representing the summation of the values of X and Y.

It must be understood that each pair of these coördinates as functions of our agents heat and cohesion represents, during expansion in the solid condition, the simultaneous development of equal units of energy from a common point of origin under different denominations or generic methods of change, but likewise summed in $C\,O$.

Viewed from this point of equality they are then comparable values, when a determination of their relative variations is sought under the various conditions of expansion in a solid body as an aid towards the location of their true and independent points of origin.

These various descriptions of each other in their own terms are then known from experiment under various conditions of expansion, and therefore can all be utilized to locate individual points of origin.

A curve can be drawn through a number of points C, each of which expresses a similar result, or certain relations that have been developed under similar methods by the antagonism of the equal energies of heat and cohesion, when the body is expanding.

The line uniting these points becomes the locus of an equation fully describing this given sequence of conditions.

It determines the law governing these relations of our agents geometrically, expressing a common property met with at all of these temperatures or stations.

The following expresses the general equation of any curve of two variables:

$$X^n+AX^{n-1}Y * * +BXY^{n-1}+CY^n * * +DX^2+EXY+FY^2+GX +HY+M = 0,$$

and the determination of the different coefficients and exponents, from A to n inclusive, define its application to any true series of conditions.

The determination of n, or of the degree of the equation is usually the most difficult.

In the present instance, however, where we desire to cover precisely the sequence of conditions named, under expansion in the solid state, and where the relation of this expansion to temperature is known to be measured by an equation of the third degree the question is practically decided for us.

In fact numberless experiments, at great varieties of temperature, have pointed with uncommon precision to a general law showing that the release of cohesive stress by heat is expressed through a lineal expansion in three directions each increasing directly with the temperature. The change then is cubical.

These expansions may be the result of many individual ones, but according to unmistakable evidence they can be summed by their general movement relatively to three rectangular axes.

In this choice of the third degree we are guided by practical results, and we are forced to recognize that the application of our stress is limited by cubical conditions in that it increases or decreases in all directions simultaneously.

This determination immediately fixes the number of terms in the equation, for the number of points on the curve, or of independent ordinates required is then equal to $1/2\,n\ (n+3)$.

In our case nine independent points are required to describe the locus

Our tables of the tests of iron and copper furnish us with this number. Our equation then becomes definite and as follows:

$$X^3+AX^2Y+BXY^2+CY^3+DX^2+EXY+FY^2+GX+HY+M=0.$$

We are thus able to construct nine independent equations by inserting in each the numerical values of one pair of our coördinates as values of X and Y.

We can thus impress, in their own terms, the general properties of all our geometrical points algebraically upon the general equation, and under these conditions, as stated, define the common property they unite in presenting.

We can now combine these equations and determine the coefficients.

It is not proposed to reproduce these calculations here, but simply to record the results for iron and copper.

EQUATION A.

For Iron.

$$X^3+0.793383\,X^2\,Y+0.20407\,X\,Y^2+0.01756\,Y^3-45.99\,X^2 -24.1858\,X\,Y-3.1302\,Y^2+703.9\,X+184.812\,Y-3587.2=0.$$

EQUATION B.

For Copper.

$$X^3+0.366455\,X^2\,Y+0.110136\,X\,Y^2+0.035922\,Y^3-10.2683\,X^2 -3.69415\,X\,Y+1.62304\,Y^2+60.4085\,X+5.0554\,Y+274.05=0.$$

It is claimed for these formulæ that each determines a locus or path, impressed upon it by the algebraic law, which was expressed by our experimental data representing the respective struggles of cohesion vs. heat when recorded geometrically.

There are two tables herewith submitted, showing numerical results obtained by extension with various values of coördinates. Each sheet shows determinations from one formula. They are presented in horizontal lines, the first two columns giving the values of X and Y used in each extension, while the other columns contain the calculated values of each term, as indicated at the head of the same.

The main question naturally is: Do they truly represent the experimental tests?

This is readily proved by a comparison of results calculated from our equations with the original data chosen to express its loci. In the tables for iron, five determinations have been made of values of Y, for the given values of X, thus chosen.

In the table for copper there are six. These special solutions are underscored for better identification.

The original results and the calculated ones are placed side by side, in the following schedule.

TABLE III.

	Iron.			Copper.	
	Original	Calculated		Original	Calculated
X	Y	Y	X	Y	Y
2.74	38.665	38.66	2.74	23.0584	23.05
4.79	47.01	47.1	4.28	20.7385	20.73
7.57	31.63	31.63	4.79	19.2622	19.4
10.94	11.60	11.60	6.44	14.13	14.09
16.44	1.7575	1.75	7.00	12.0916	11.98
			7.57	9.842	9.74

Comparison of the summations of the positive and negative terms in the last column in the table, as well as of the other solutions there appended, will enable the reader to judge of the accuracy with which these formulæ follow the loci as described geometrically by the original data. We find there such results as $11174.42 - 11174.4 = 0$ and $17044.0 - 17043.6 = 0$.

As the accuracy of the formulæ is thus established, we may regard them as being as true to the facts as these latter are represented by the experimental tests.

Other determinations are also recorded on the tables where X is assumed and the corresponding value of Y calculated.

These range from $X = 0$ to $Y = 0$ and we turn our attention to this latter point, for here we reach an intersection of the abscissa by the curve.

Naturally the point $Y = 0$ falls at the melting-point. In accordance with known facts we have vested the material particles of our specimen with cohesive stresses, recognizing that they react upon each other in various ways not simply as atoms but as molecules, or in mass, as indicated by the cubic formulæ.

Further we note that as we raise the temperature they in-

TABLE IV.
Results from Formula for Iron.

$x = \frac{\text{temp. } a.\ c.}{100}$

$y =$ Kilogr. per sq. mm.

$x^3 + Ax^2y + Bxy^2 + Cy^3 - Dx^2 - Exy - Fy^2 + Gx + Hy - m = 0.$

	x^3	$+ .79338x^2y$	$+ .204076xy^2$	$+ .0175276y^3$	$-45.997x^2$	$-24.1958xy$	$-3.1302y^2$	$+ 703.9x$	$+184.812y$	$-3587.2 = 0.$	Summation.
log. coef.	=	$\overline{1}$.8994829	$\overline{1}$.3097930	$\overline{2}$.2437228	1.6627293	1.3835603	0.4955728	2.8475108	2.2667297		
$x=0.$ $y=45.$	0.	0.	0.	1597.2	0.	0.	—6338.6	0.	+8316.5	—3587.2=0.	9913.7 = 9925.8
$x=1.$ $y=43.7$	1.	+34.671	+389.68	+1462.7	—45.997	— 1056.9	—5977.7	+ 703.9	+ 8076.3	—3587.2=0.	10668.25 = 10667.8
$x=2.$ $y=39.8$	8.	+126.3	+660.6	+1105.	—183.988	— 1925.2	—4935.5	+1407.8	+7355.4	—3587.2=0.	10631.8 10663.1
$x=2.74$ $y=38.66$	20.5108	+230.304	+835.949	+1013.16	—345.327	— 2562.29	—4679.6	+1928.69	+7145.75	—3587.2=0.	11174.42 = 11174.41
$x=3.74$ $y=50.$	52.312	+554.87	+1908.1	+2190.9	—643.387	— 4522.8	— 7825.5	+ 2632.59	+ 9240.6	—3587.2=0.	16579.37 = 16578.88
$x=4.79$ $y=47.10$	109.90	+857.401	+2168.6	+1831.5	—1055.4	— 5456.6	— 6944.4	+ 3371.7	+ 8705.	—3587.2=0.	17044.1 = 17043.6
$x=7.57$ $y=31.63$	433.8	+1438.3	+1546.4	+ 552.36	—2635.9	— 5792.0	— 3132.6	+ 5328.5	+5846.6	—3587.2=0.	15145.96 = 15147.7
$x=10.94$ $y=11.6$	1309.3	+1101.4	+ 300.39	+27.355	—5505.1	— 3069.1	— 421.17	+ 7700.7	+ 2143.7	—3587.2=0.	12582.84 = 12582.57
$x=16.44$ $y=1.75$	4443.3	+376.86	+ 10.86	+ .09515	—12431.	— 698.8	— 9.6685	+11572.	+ 324.8	—3587.2=0.	16727.91 = 16726.46
$x=17.25$ $y=0.$	5133.	+ 0.	+ 0.	+ 0.	—13687.	— 0.	— 0.	+12142.	+ 0.	—3587.2=0.	17275. = 17274.2
$x=19.25$ $y=—5.4$	7133.	—1587.5	+ 114.56	— 2.76	—17045.	+ 2514.1	— 91.275	+13550.	— 997.98	—3587.2=0.	23311.66 = 23311.71
$x=20.25$ $y=—8.1$	8303.	—2635.2	+ 276.13	— 9.31	—18861.	+ 3967.	— 204.37	+14254.	— 1497.	—3587.2=0.	26800.13 = 26795.08
$x=27.$ $y=—26.15$	19682.	—1512.4	+3767.9	— 313.42	—33531.	+17076.	— 2140.5	+19005.	— 4832.9	—3587.2=0.	59530.9 = 59529.
$x=30.$ $y=—38.5$	27000.	—27490.	+9074.7	— 1000.	—41397.3	+27935.	— 4639.8	+21117.	— 7115.	—3587.2=0.	85126.7 = 85229.
$x=40.$ $y=—61.$	64000.	—77434.	+30375.	— 3978.	—73594.	+59014.	—11647.	+28156.	—11274.	—3587.2=0.	181545. = 181514.
$x=45.$ $y=—74.$	91125.	—118890.	+ 50288.	— 7103.	— 93144.	+80539	—17141.	+31675	—13676.	—3587.2=0.	253629. = 253548.
$x=60.$ $y=—114.5$	216000	—327033.	+160530.	—26310.	—165589.	+166150.	—41038.	+42234.	—21160.	—3587.2=0.	584914. = 584717.

TABLE V.

RESULTS FROM FORMULA FOR COPPER.

$x = \frac{\text{temp. } a.\ c.}{100}$

$y =$ Kilo per. sq. mm.

	x^3	$+Ax^2y$	$+Bxy^2$	$+Cy^3$	$-Dx^2$	$-Exy$	$-Fy^2$	$+Gx$	$+Hy$	$+m = 0.$	
	x^3	$+.366455x^2y+$	$.110136xy^2+$	$.035922y^3-$	$19.2683x^2-$	$3.6915xy$	$-1.62304y^2$	$+60.4058x$	$+5.0554y$	$+274.055=0$	Summation.
$x=0.$ $y=20.8$				+323.25			—702.17		+105.15	+274.055=0	
$x=2.74$ $y=23.05$	20.570	+63.4382	+160.450	+440.405	—144.659	—233.397	—862.952	+165.519	+116.57	+274.055=0	1241.=
$x=3.672$											1241.=
$y=21.89$	49.552	+106.892	+192.125	+371.806	—259.948	—295.701	—770.837	+221.88	+110.172	+274.055=0	1326.48= 1326.48
$x=3.74$ $y=21.72$	52.313	+111.33	+194.33	+368.08	—269.51	—300.08	—765.65	+225.92	+109.80	+274.055=0.	1335.82= 1335.24
$x=4.23$ $y=20.73$	75.687	+135.98	+200.36	+320.40	—344.77	—324.06	—698.03	+255.52	+104.84	+274.055=0.	1366.84= 1366.86
$x=4.79$ $y=19.4$	109.9	+161.95	+195.74	+256.73	—442.09	—340.84	—602.19	+289.35	+ 97.367	+274.055=0.	1385.10= 1385.12
$x=5.34$ $y=17.82$	152.27	+185.86	+186.05	+202.11	—549.44	—350.85	—513.42	+322.58	+ 89.913	+274.055=0.	1412.83= 1413.71
$x=6.44$ $y=14.09$	267.09	+214.75	+141.62	+101.35	—790.12	—336.16	—324.06	+389.02	+ 71.434	+274.055=0.	1459.32= 1459.34
$x=7.01$ $y=11.91$	344.47	+217.74	+112.88	+ 63.506	—946.83	—313.12	—237.28	+423.45	+ 61.127	+274.055=0.	1497.23= 1497.22
$x=7.57$ $y=9.71$	433.79	+206.68	+ 80.759	+ 34.246	—1104.2	—275.23	—157.21	+457.28	+ 49.755	+274.055=0.	1536.57= 1536.64
$x=8.14$ $y=7.73$	539.34	+187.67	+ 53.569	+ 16.592	—1276.7	—232.44	— 96.98	+491.72	+ 39.078	+274.055=0.	1602.02= 1606.12
$x=13.00$ $y=0.$	2197.	+ 0.	+ 0.	+ 0.	—3256.35	0.	0.	+785.31	+ 0.	+274.055=0.	3256.36= 3256.35
$x=14.736$ $y=-5.734$	3200	—456.3	+ 53.61	— 6.772	—4184.3	+312.09	— 53.361	+890.2	— 28.987	+274.055=0.	4729.95= 4729.75
$x=23.00$ $y=-30.43$	12167.	—5899.6	+2345.6	—1012.2	—10192.	+2582.2	—1502.9	+1389.3	—153.83	+274.055=0.	18758.1= 18760.5
$x=33.$ $y=-59.46$	35937.	—2372.8	+12849.	—7551.3	—20983	+7244.7	—5738.	+1993.4	—305.9	+274.055=0.	58298.1= 58306.2
$x=40.$ $y=-79.69$	64000.	—46724	+27912.	—18178	—30829	+11775.	—10308.	+2416.	—402.25	+274.055=0.	106377.= 106441.
$x=50.$ $y=-108.54$	125000	—99438	+64876	—45934	—48171	+20048.	—19121	+3020	—548.71	+274.055=0.	213218.= 213212.7
$x=60.$ $y=-137.38$	216000	—181230	+124720	—93140	—69365	+30450	—30630	+3624.	—694.50	+274.055=0.	375068.= 375059.
$x=70.$ $y=-166.70$	343000	—289440	+212960	—164910	— 94415	+42978.	—44832.	+4228.6	—840.2	+274.055=0.	603440.= 603437.

crease their distance apart until the melting-point is reached, where this cohesive tendency as a mass becomes zero.

Under continued change from this point two events are possible, either the line must curve upwards again, or it must cross the abscissa, the values of Y becoming negative.

The second condition ensues, for by assuming values of X greater than that of the melting-point and calculating new values of Y from the formula, we find them taking a negative form. Several of these solutions are given in the tables.

What does this indicate? Apparently, that in lieu of the original attractions between the particles in mass, or as we may say in molecular form, a condition of repulsion begins. In

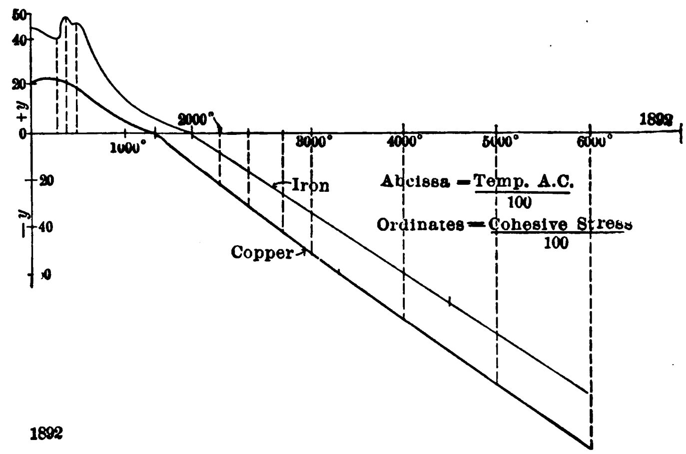


CHART B.

place of being held together, our particles under increasing temperature are subjected to a slowly increasing repulsion, resulting from a motion actuated by heat energy.

We know that in the liquid form particles tend to separate from each other if permitted to do so, and here we find the point of origin of the stress causing this effect and destroying the solid form.

A peculiar result is presented. The lines representing the determinations of $-Y$ for values of X greater than that at the melting-point are practically straight when mapped.

This result occurs in both formulæ. Their extensions are shown on Chart B, together with the original curves, the loci of which we forced upon our formulæ, as explained.

Taken as a mathematical question this fact means that when reckoned from the melting-point as a new point of origin a constant relationship is maintained between the new abscissa value expressed as $(X - M\ P)$, and the ordinate $-Y$. This is a well known condition of an intersection of a straight line with the coördinate.

One peculiarity of the situation lies, however, in the fact that our complicated formulæ forced, as we have explained, to occupy the loci expressed by two independent sets of experimental results of our struggle of cohesion vs. heat, should yield simple and parallel courses in both cases.

It is a feature then of somewhat common occurrence, though to what extent we are as yet hardly able to judge, though both formulæ follow a similar course.

Our attention is naturally attracted by the fact that in the term $(X - M\ P)$ this value of the melting-point or M. P. is a constant in each case, and that when this value is deducted from the temperature a. c. we find this simple proportion existing between the changes of temperature and the prevailing stress.

In both cases under consideration the melting-point assumes such a position, and we can bear this in mind for future service, especially as every material passes through this stage at some temperature.

There is, however, another leading feature connected with this straight line.

It relates to the actual values of the calculated results from this proportion $\frac{X - M\ P}{-Y}$. The following figures are taken from the tables submitted, and when reduced to their simplest terms are as follows, in the case of iron:

$X - M\ P = 19.25 - 17.25 = 2.00$ when $-Y = 5.4$ and

$$\frac{X - M\ P}{-Y} = \frac{1}{2.70}$$

$X - M\ P = 60.00 - 17.25 = 42.75$ when $-Y = 114.5$ and

$$\frac{X - M\ P}{-Y} = \frac{1}{2.678}$$

In the case of copper:

$X - M\ P = 33.00 - 13 = 20.$ when $-Y = 59.4$ and

$$\frac{X - M\,P}{-Y} = \frac{1}{2.97}$$

$X - M\,P = 60.00 - 13 = 47.00$ when $-\,Y = 137.$ and

$$\frac{X - M\,P}{-Y} = \frac{1}{2.92}$$

These values recall the rate of gaseous expansion determined by Regnault. For we find $\frac{X - M\,P}{-Y}$ equal approximately to $\frac{1}{2.70}$ especially in the formula for iron.

The unit of temperature adapted for use in these formulæ was 100° C expressed by 1. Changing this unit to that covering the ordinary degree the ratio becomes $\frac{1}{270}$ per unit degree centigrade. Regnault's result is $\frac{1}{273}$.

Our two formulæ expressing these struggles of Cohesion vs. Heat, though similar in general form, vary greatly in detail.

They are derived from experimental sources entirely independent and distinct but still both point unmistakably in the direction indicated, though that of iron is apparently the best approximation to the truth.

Our formulæ then recognize no liquid state as such, other than that occurring at the melting-point proper, where we find Y equals zero. They pass from conditions of molecular attraction, as found in the solid and as embodied in our cubic formulæ, through zero, to a growing state of repulsion complying with what we know to be the fact, that similar laws control the expansion of all material in the gaseous state.

It is only of recent date that the difficulty has been recognized of determining just where the liquid state originates when compressing gases. The passage of the material from gas to vapor and thence to liquid was so gradual that doubt was expressed regarding the existence of a dividing line between these states.

Neither do our formulae recognize a limit to the struggle under discussion, for we find the values of $-\,Y$ increasing indefinitely with those of X.

Still, it is possible that the values of $-Y$ represent a repulsion between the molecules as nuclei, a stress due at this state of the conflict between cohesion and heat, their former attractions having been neutralized by their present increased distance apart.

Though we know at the same time that in order to reduce the struggle to conditions occurring in Nature, some limit must be recognized where cohesion can be exhausted.

The problem is complicated by the resistance of an atmosphere, under the pressure of which the material must be gasified in order to disperse.

This physical limit is in no way connected with the amount of cohesion present, but at the same time the dispersal forms the limit of our struggle.

By a reduction of pressure the dispersal can occur at a lower temperature, for the boiling-point is dependent upon the pressure.

In choosing our limit to this struggle then, two possible cases may arise, namely: A, When gasification takes place under full atmospheric pressure; B, when gasification takes place under reduced pressure.

If the pressure is sufficiently reduced evidently the evaporation from the fluid state may be brought as low as the melting-point. Then the latter and the boiling-point must coincide, and the liquid condition would be found at this one station only.

This physical state, or the one due at this double station, seems to be the one represented by our formula, for in expressing the rate of change by degrees centigrade the intersection of the curve with the abscissa falls at the melting-point, indicating its arrival at the fluid condition. But, in passing from this station it assumes a rate of increase, as expressed by the ratio of the ordinates, which we must recognize as the rate of change of the gaseous condition.

It is also evident that changes of atmospheric pressure could not alter either the experimental temperature or the cohesive strength of the specimen during the test.

We can conclude therefore, that our tests are absolutely unaffected by the atmospheric pressure, and that the struggle ensuing between heat and cohesion, as covered by our formula, must be the one occurring where M P and B P coincide.

But at the same time it is clear that this condition is not the one usually occurring where energy is developed under change and we must be prepared to consider both cases.

We must recognize that in the computations of chemical energy the atmospheric conditions must be reckoned with. Still, we must bear in mind that, under suitable conditions, gasification or evaporation can occur at low temperatures.

Then the energy expended from this station, to any other under atmospheric pressure, must be precisely the same as that spent when the change takes place under 760 mm. of mercury.

For instance, when water is evaporated in a vacuum pan, the boiling-point is lowered, but the energy expended is the same as when the evaporation takes place in the open air, if we allow for the energy required to raise the temperature of the product to the boiling-point under atmospheric pressure.

Our formula of the third degree measures cohesion in degrees of physical change, thus expressing the rates of energy consumed under each unit, It does not measure the total energy developed, but simply indicates that from the melting-point upwards $-Y$ exists and grows at a given rate.

The energy required for the total change to a fixed station or for evaporation remains constant, however, for as the sensible energy is reduced by changes of the character mentioned, just so the latent energy must be increased.

When evaporation occurs at the melting-point then, the sensible energy of the liquid condition becomes zero, and the latent energy a maximum. But, as stated, the total energy developed between certain fixed stations can be calculated equally well by method A or method B. The results must be identical.

The results of our study of the struggle of cohesion vs. heat seem to point to a continuation of the conditions of this struggle even when the melting-point is passed and the gaseous condition begun. It is now the cohesion of the liquid that remains to be overcome, to the boiling-point of each solution, through the constant increase of our negative stress, or of $-Y$, to this fixed limit of temperature which is determined by the internal condition relatively to a constant atmospheric pressure.

The ratio of expansion occurring at this stage $\frac{X - M\,P}{-Y}$ indicates an approach to constancy in the growth of our ordi-

nates. In this connection it may be noted that, although many experimental results attained in this direction are not any closer than ours, such a constancy is an accepted fact.

A comparative table of our determinations and of accepted experimental results is given on the following page. It will be seen that while Regnault's result stands at 1/272.9 other experimental values fall as low as 1/256.2 while our values range from 1/270 to 1/297.

We have here our first comparison between calculated and experimental results, and the relative values thereof must be represented by the relative accuracy reached.

In order, however, to confirm our first results a trial has been made with a third metal. Selection was made of an alloy of which a series of tests presented themselves.

The alloy is known to the trade as Muntz-metal, and is composed of 60% copper and 40% zinc approximately.

The following pairs of experimental values, expressing the relationship of our ordinates X and Y, in the solid state, were used to determine the coefficients.

X	Y	X	Y
2.99	33.6	3.305	33.40
5.34	25.86	4.507	38.25
3.117	33.55	3.673	33.00
4.7844	29.5	15.00	0.
		4.2288	31.80

With these data the equation becomes:

$$X^3 + 0.0008256\,X^2\,Y - 0.0615782\,X\,Y^2 + 0.02374\,Y^3 - 7.35231\,X^2 + 7.13414\,X\,Y - 1.32687\,Y^2 - 153.3091\,X + 0.178567\,Y + 578.878 = 0.$$

Calculated from this the line of $-Y$ is again practically straight after passing the melting-point and we have the approach to constancy confirmed. It ranges from 1/285 to 1/280 as an approximation of 1/273.

Comparison of the results of these formulæ, or of $\dfrac{X - M\,P}{-\,Y}$ with accepted constants is made in the following table.

TABLE VI.

Name of Formula.	Temp. of Calculation.	Value of $\frac{X-MP}{-Y}$	Coefficient of Expansion.	Source and letter in Chart C.
Iron	1925 a.c.	1/270	0.0037037	Formula A
Iron	6000 a.c.	1/267.8	0.003725	Formula A.
Copper	3300 a.c.	1/297	0.0033667	Formula B
Copper	6000 a.c.	1/292	0.0034246	Formula B
Muntz	1700 a.c.	1/285	0.0035087	Formula C
Metal	6000 a.c.	1/280	0.0034965	Formula C
Suggested		1/271.44	0.003663	$100^3\sqrt{2\times 10}$
theoretical	(when the uni	t is 10, 20	is its double).	D.
Air		1/272.9	0.003667	Regnault. E.
H			0.003661	Experimental
CO			0.003669	Experimental
CO^2			0.00371	Experimental
CN			0.003877	Experimental
SO^2			0.003903	Experimental

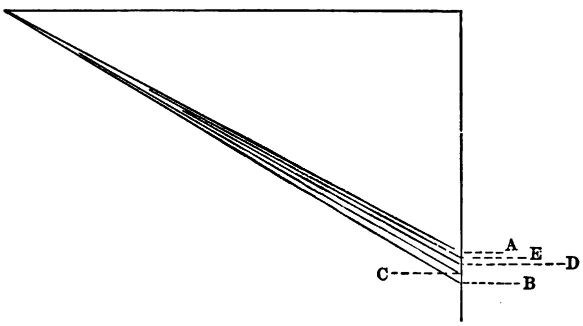


CHART C.

Chart C presents the variations existing between the results and their individual approach to Regnault's value, or to constancy.

* * *

The point we have brought out most markedly thus far in our study of Cohesion vs. Heat is that at the melting-point an important change takes place. Owing to the gaseous expansion which originates here the particles are able to move freely.

The gaseous condition can thus follow immediately if no

resistance is offered by the surrounding pressure, for the rate of increase, as shown, is very closely 1/273 per degree of change.

In connection with the above the fact is of importance that, when this point of origin is reached the same conditions must result between heat and cohesion in all bodies, regardless of the mass held per unit volume, for here Y equals zero.

It follows then, that if we had the data to construct curves and equations for all materials, similar to those shown on Chart D, all portions of the curves lying below the abscissa would be composed of nearly straight lines, intersecting the abscissa at the same angle but originating at different points, as indicated on the chart.

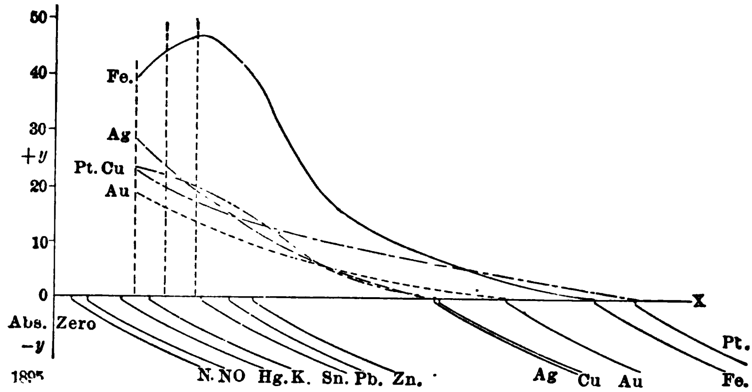


CHART D.—Showing constant relationship in all material under gaseous tension.

As these lines are very nearly straight and bear an almost constant relation to a well known portion of the abscissa, the question arises: why cannot the equation for the one be used to calculate a new and similar equation, with its zero or melting point at any fixed distance from the absolute zero?

Mathematically we certainly could, in this manner, get equations for the curves, similar to the chosen base, originating at any desired point.

A second question arises: would these equations when used with the values of $+Y$ yield results in any way comparable with those that had been determined experimentally by rupture?

To answer this question in the affirmative would mean to

assert that, in the struggle of heat and cohesion, these agents were always obeying similar laws, and that one law reigned in all material, not simply in the repulsive state but, in the solid state also where fixed conditions prevail.

As the equation for iron approximates most closely to the determination of the correct value of the coefficient of the gaseous expansion, it naturally is the proper one for our new base. Our study tends in this direction, and we shall try to reproduce the equation for copper, with its divers rupture stresses from that for iron, and possibly even more, and contend that a successful outcome will prove all we have thus far claimed for these methods.

At first sight it appears singular that this proposition should be made in good faith, that, by any method it should be possible to determine the rupture stresses of copper specimens from a series of tests made upon iron samples.

When, however, it is realized that in each case a common measure of internal stress exists, namely heat, and that a similar and known relationship is maintained between the internal and the external agents, it becomes evident that the conditions are in reality not so severe as we imagine.

There are various methods by which this mathematical change can be performed. The following offered fewest chances of error and was preferred.

It consists in regarding the formula for the gaseous expansion, or that representing the part of the line below the abscissa as an independent equation, because of the constancy of the term $\frac{X - M P}{-Y}$ throughout this period.

In order to accomplish this $-Y$ is inserted for $+Y$ in the equation; thus Y^3 and Y become negative and Y^2 remains positive, resulting in the change of signs in several terms.

It is for the purpose of effecting this change at once and thus avoiding chances of error that this proposed course is followed.

These changes in the equation for iron can be seen in the following where the original alphabetical coefficients have been retained for the sake of simplicity.

The original equation for the solid condition is:

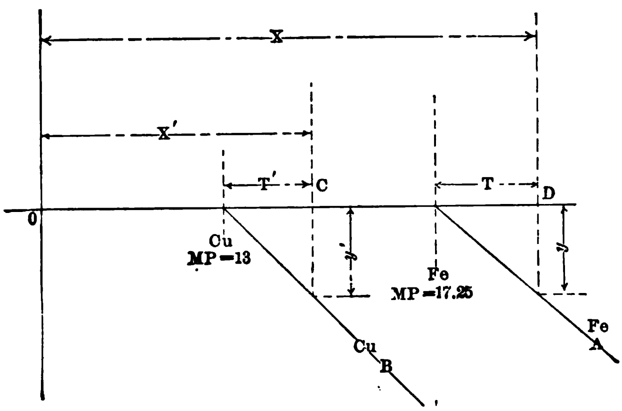
$X^3 + A X^2 Y + B X Y^2 + C Y^3 - D X^2 - E X Y - F Y^2 + G X + H Y - M = 0.$

Substituting $-Y$ for $+Y$ the equation becomes:
$X^3 - A X^2 Y + B X Y^2 - C Y^3 - D X^2 + E X Y - F Y^2 + G X - H Y - M = 0.$

Naturally by reversing these signs at any time the original formula can be restored.

As we have now the formula representing our struggle for conditions of change in the gaseous state, we can turn our attention to methods whereby the zero, or the melting-point, can be transferred mathematically to any point upon the abscissa, and study the results following the transfer.

Let A in the adjoining sketch be the line of iron, as represented by the formula originating at $M P = 17.25$, while B is a similar line originating from the melting-point of copper at 13.00.



We desire to determine a formula for B from that of A by changing the value of the point of intersection. The condition of the change is the constancy of the term $\frac{X - M P}{+Y}$ therefore

$$\frac{X - M P}{Y} = \frac{X' - M P'}{Y'}$$

We assume a value of X' equal to $O C$, then $O C - 13.00 = T'$ and take $O D$ so that $T = T'$, then $O D - 17.25 = T$.

If the lines A and B are parallel, which is a condition of the case, it follows that $Y = Y'$ and $\frac{T}{Y} = \frac{T'}{Y'}$.

Then $X - M\,P = X' - M\,P'$. By substituting the numerical values of $M\,P$ and $M\,P'$, we can determine the relative values of X and X'.

We have $T = X - 17.25$ and

$T' = X' - 13.00$ and under the conditions given above: $X - 17.25 = X' - 13.00$, and $X - X' = 4.25$.

Therefore in order to determine the equation of a line B originating at 13.00 and parallel to A, intersecting the abscissa under similar conditions or proportions of ordinates $\frac{T}{Y} = \frac{1}{2.73}$ we must insert $X' + 4.25$ for X throughout equation A.

This will result in a similar equation, with some coefficients altered, supposedly expressing the conditions of our struggle between the internal and external agents in the gaseous molecule of a copper specimen.

We propose to test this question numerically, and note that when we desire to revert to the general form of the equation for copper, we must simply reverse the changes made by the introduction of $-Y$ for $+Y$ in the equation.

This change of equation from line A to line B is shown upon the adjoining page. We have given there, first that of A after $-Y$ has been inserted, and made ready for the substitution of $X'+4.25$.

In the first column we find this equation repeated, by placing each succeeding term vertically under its predecessor; the numerical coefficients for convenience being indicated by letter instead of by the long numeral.

This vertical arrangement is made in order to determine a position for each substitution so that similar terms can be conveniently added or subtracted.

Thus the line X^3 has the value of $(X'+4.25)^3$ extended and its terms so placed that the extensions of the other terms can be suitably located. They follow in their proper order. On the thirteenth line the summation is made and represents for us the equation of the line B.

We note that the first three terms suffer no change. All the other coefficients are, however, reduced, the last term falling from 3587 to 1349.69 and the whole extension equalling zero as before.

TABLE VII.

FORMULA FOR IRON WITH VALUES OF $-y$ INSERTED.

DETERMINATION OF NEW EQUATION FOR Cu BY TRANSFERRING $M\ P$ FROM 17.25 TO 13.00

$x = \frac{\text{Deg. A. C.}}{100}$ $y =$ Klgr. per sq. mm.

Formula. A	x^3	$-.79338x^2y$	$+.204076xy^2$	$-.0175276y^3$	$-45.997x^2$	$+24.1858xy$	$-3.1302y^2$	$+703.9x$	$-184.812y$	$-3587.2=0.$	
Iron $x=T+17.25$. Cop. $x'=T+13$. Substitution of $x'+4.25$ for x^o											
x^3	x_1^3				$+12.75x_1^2$			$+54.1875x_1$		$+76.765$	
$-A\ x^2\ y$		$-.79338x_1^2y$				$6.7437x_1y$			$-14.3304y$		
$+B\ x\ y^2$			$+.204076x_1y^2$				$+0.86729y^2$				
$-C\ y^3$				$-.0175276y^3$							
$-D\ x^2$					$-45.997x_1^2$			$-390.974x_1$		-830.82	
$+E\ x\ y$						$+24.1858xy$			$+102.789y$		
$-F\ y^2$							$-3.1302y^2$				
$+G\ x$								$+703.9x_1$		$+2991.57$	
$-H\ y$									$-184.812y$		
$-M$										-3587.2	
Formula B	x_1^3	$-.79338x_1^2y$	$+.204076x_1y^2$	$-.0175276y^3$	$-33.247x_1^2$	$+17.4421x_1y$	$-2.26291y^2$	$+367.113x_1$	$-96.3534y$	$-1349.69=0.$	copper gas.
$x=13.$ $y=0.$	2197				-5618.74			$+4772.469$		$-1349.69=0.$	$6969.54=$ 6968.43
$x=23.$ $y=27.3$	12167.	$-11457.$	$+3498.1$	-3566.2	$-17587.$	$+10951$	-1691.1	$+8443.3$	-2630.4	$-1349.69=0.$	$35059.=$ $35071.$
Determinations from "General Formula" with altered signs.											
	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.017276y^3$	$-33.247x^2$	$-17.4421xy$	$-2.26291y^2$	$+367.113x$	$+96.3534y$	$-1349.69=0.$	copper solid
$x=6.44$ $y=14.1303$	267.	$+464.95$	$+262.38$	$+49.45$	-1378.87	-1587.1	-453.06	$+2364.2$	$+1361.5$	$-1349.69=0.$	$4769.5=$ 4768.7
$x=2.74$ $y=23.0584$	20.57	$+137.34$	$+297.29$	$+214.87$	-249.6	$-1102.$	-1206.4	$+1005.9$	$+2221.7$	$-1349.69=0.$	$3897.6=$ 3907.7
$x=2.88$ $y=19.$	23.888	$+125.03$	$+212.17$	$+120.22$	-275.76	-954.4	-819.13	$+1057.2$	$+1830.7$	$-1349.69=0.$	$3369.2=$ 3397.98
$x=0.91$ $y=28.$	0.75	$+18.39$	$+145.59$	$+384.75$	-27.532	-444.41	-1779.0	$+334.07$	$+2697.8$	$-1349.69=0.$	$3581.35=$ 3599.63

These two last tests are from Prof. Dewar's determinations with wires from Rhielie's Digest of Physical Tests, Oct. 1896, p. 312. The others $x=6.44$ and 2.74 are taken from table in the text.

In order to test this formula, let us first make sure that it fulfils the conditions we have tried to impress upon it, namely, that Y must equal zero at 13.00 and that $\frac{X-MP}{Y}$ must be equal to $\frac{1}{2.73}$. Immediately below this formula the extensions obtained by inserting these values are presented.

In the first $X = 13.00$ and $Y = 0$ are used.

The test is made by summing the negative and positive terms, if they are equal the accuracy of the formula is established. The summation is shown at the right hand end of the same line. The approach of 6969.54 and 6968.45 to equality is all that could be desired.

In the second, X is taken at 23 and Y at 27.3, then:

$\frac{X-MP}{Y} = \frac{23-13}{27.3} = \frac{10}{27.3} = \frac{1}{2.73}$ and the summation is $35059.4 = 35071.8$ with which no fault can be found.

We can therefore accept this equation as representing the gaseous condition reigning in a copper specimen, for we have proved that it describes the locus of that condition for that metal. We propose to show further that by changing the signs, obtaining the general equation and inserting the values of X and Y selected from those given in the original tables as experimental rupture tests, equally exact summations can be obtained.

These summations show that if, for instance, the value given for X was inserted, the equation would be solvable for the experimental value of Y, as claimed.

Immediately below the last mentioned summations of the equation with X and Y equal respectively to 23 and 27.3 we find the general formula obtained by reversing the signs caused by the introduction of $-Y$ for $+Y$, and below it again are two extensions, the first substituting values of X at 6.44 and Y at 14.303; the second at X at 2.74 and Y at 23.0584, both taken from the table of experimental ruptures of copper already given in the text. The first yields a summation of

$$4769.49 = 4768.72 \text{ and the second}$$
$$3907.2 = 3879.67.$$

For further proof two summations are presented from tests by Professor Dewar on copper wires, one occurring at $-182°$ C.

The first test with X at 2.88 and Y at 19 yields 3369.2 = 3397.98 and the one at low temperature with X at 0.91 and Y at 28 yields 3581.35 = 3599.63.

Greater accuracy was hardly to be expected under this severe test. It is claimed that this again is satisfactory proof of the accuracy of our methods thus far, and that we have shown the general formula to describe the locus of the line of copper both above and below the abscissa.

On Tables VIII and IX several equations are shown which have been obtained by transferring that of iron with its melting point at 17.25 to the following melting-points of metals expressed in the same scale.

Muntz metal	15.00	Zinc	6.906
Silver	12.335	Bismuth	5.422
Tin	5.047	Lead	6.007

Below each of these formula are to be found several extensions, each with a pair of experimental values of X and Y, or of the rupture tests at stated temperatures of the metal in question. These values are given on the left side of the sheet next the individual extensions, while the equality of the corresponding summations, negative and positive is shown on the right.

Thus eighteen independent tests show that in six different metals the struggle of cohesion vs. heat can be calculated from experimental data taken from the iron specimen.

Some of these tests are at extremely low temperatures as made by Professor Dewar; others are taken from quoted sources, where the laboratory temperature is sometimes estimated at 300 a.c.

These results are summarized on page 35 and it is difficult to believe they could be other than convincing.

Thus the correctness of the equation of iron, as an individual specimen or kind is shown, as well as the fact that, the correct formula for the conditions reigning in either material, simple or compound, can be calculated therefrom.

There is perhaps another indication of the value and the accuracy of our equation worth recording.

It tends to show how the equation, through its many terms, truly interprets the mathematical conditions that are covered

TABLE VIII.

GENERAL FORMULA. DETERMINATION OF A NEW EQUATION FOR MUNTZ METAL BY TRANSFERRING ZERO OF STRESS FROM 17.25 TO 15.00

$x = \frac{\text{Deg. } a.\,c.}{100}$

$y =$ Kilo. per sq. mm.

	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.0175276y^3$	$-39.247x^2$	$-20.6156xy$	$-2.67103y^2$	$+512.101x$	$+134.41y$	$-2244.89=0$	
$x=15.$ $y=0.$	3375.				—8830.58			+7681.515		—2244.89 =0	11056.51 = 11055.48
$x=16.$ $y=-2.74$	4096.	—554.48	+ 24.3354	— 0.3566	—10047.	+ 900.49	—19.907	+8193.6	—336.939	—2244.89 =0	13214.4 = 13183.5
$x=2.99$ $y=33.6$	26.97	+239.76	+690.95	+664.88	—352.99	—2077.3	—3015.5	+1535.8	+4516.2	—2244.89 =0	7674.5 = 7670.18
$x=4.7844$ $y=29.5$	109.52	+535.74	+849.70	+449.97	—898.38	—2909.7	—2324.5	+2450.1	+3965.1	—2244.89 =0	8356.1 = 8357.47
$x=4.507$ $y=38.25$	91.55	+616.43	+1345.7	+980.88	—797.22	—3554.	—3907.9	+2308.	+5141.2	—2244.89 =0	10483.7 = 10484.

Data tests 1, 2, 3, Thurston Materials, p. 532. NEW EQUATION FOR SILVER. Zero of stress at $M\ P$ transferred to 12.335. $x=x'+4.915$

	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.0175276y^3$	$-31.252x^2$	$-16.3869xy$	$-2.12717y^2$	$+324.2217x$	$+85.105y$	$-1119.96=0$	
$x=M\ P$ $y=0.$	1876.8				—4755.06			+3999.15		—1119.96 =0	5875.02 = 5875.9
$x=13.335$ $y=-2.73$	2371.76	—385.15	+ 20.281	— 0.35662	—5557.3	+596.56	— 15.853	+4323.3	—232.33	—1119.96 =0	7310.94 = 7311.4
$x=2.73$ $y=28.32$ } 1	20.346	+167.45	+446.83	+398.11	—232.92	—1266.9	—1706.	+ 885.1	+2410.2	—1119.96 =0	4328.05 = 4325.78
$x=3.73$ $y=23.27$ } 2	51.895	+256.86	+412.19	+220.86	—434.81	—1422.4	—1151.85	+1209.3	+1980.4	—1119.96 =0	4131.5 = 4129.05
$x=4.73$ $y=18.58$ } 3	105.82	+329.8	+333.23	+112.424	—699.198	—1440.14	—734.334	+1533.52	+1553.52	—1119.96 =0	3996.04 = 3993.6

Data tests 1 and 2, Prof. Dewar. EQUATION FOR TIN. Zero of stress transferred to 5.047. $x=x'+12.203$

	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.0175276y^3$	$-9.388x^2$	$-4.8225xy$	$-0.63986y^2$	$+28.04x$	$+7.818y$	$-29.87=0$	
$x=5.047$ $y=0.$	128.6				—239.13			+141.5		— 29.87 =0	269. = 270.13
$x=3.00$ $y=3.5$	27.	+ 24.991	+ 7.499	+0.75146	—84.495	— 50.635	— 7.838	+ 84.119	+ 27.362	— 29.87 =0	171.723 = 172.834
$x=2.88$ $y=4.5$ } 1	23.88	+ 29.61	+ 11.9	+ 1.597	— 77.86	— 62.49	— 12.95	+ 80.75	+ 35.18	— 29.87 =0	182.91 = 183.17
$x=0.91$ $y=8.70$ } 2	0.75	+ 5.715	+ 14.05	+ 11.55	— 7.76	— 38.17	— 48.42	+ 25.516	+ 68.01	— 29.87 =0	125.59 = 124.23

EQUATION FOR ZINC. Zero of stress transferred to 6.906. $x=x'+10.344$

	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.0175276y^3$	$-14.965x^2$	$-7.7715xy$	$-1.01923y^2$	$+73.21x$	$+19.537y$	$-120.9=0$	
$x=6.906$ $y=0.$	329.36				—713.72			+505.9		—120.9 =0	834.62 = 834.96
$x=3.$ $y=5.26$ } 1	27.	+ 37.55	+ 16.938	+ 2.55	—134.68	—122.63	—28.198	+219.63	+102.76	—120.9 =0	406.48 = 406.40
$x=0.$ $y=19.03$				+120.9			—369.32		+371.9	—120.9 =0	

Test (1). Die Hütte gives the breaking stress zinc 526 kil. sq. cmm. = 5.26 sq. mm. temp. estimated $273°+27=300°$ $x=3.$

TABLE IX.

LINE FOR BISMUTH.

ZERO OF STRESS TRANSFERRED FROM 17.25 TO 5.422

GENERAL FORMULA. $x = x' + 11.828$ $x = \frac{\text{Deg. A. C.}}{100}$ $y =$ Kilo. per sq. mm.

	x^3	$+.79338x^2y$	$+.204076xy^2$	$+.0175276y^3$	$-10.513x^2$	$-5.4175xy$	$-0.71638y^2$	$+35.504x$	$+9.735y$	$-41.77=0.$	
$x=5.422$ $y=0.$	159.4				—309.06			+192.5		—41.77=0.	351.9 — 350.83
$x=3.$ $y=2.2496$	27.	+16.063	+3.0982	+ .1995	— 94.615	—36.56	—3.6253	+106.51	+21.899	—41.77=0.	174.77 — 176.57
$x=2.88$ $y=1.3$ } 1	23.884	+ 8.554	+0.99	+0.038	— 87.19	—20.28	—1.210	+102.24	+12.65	—41.77=0.	148.35 — 150.45
$x=0.91$ $y=0.67$ } 2	0.75	+ 0.44	+0.083	+0.005	— 8.7	— 3.303	—0.32	+ 32.308	+ 6.52	—41.77=0.	40.106— 54.09

Tests 1 and 2 by Prof. Dewar.

EQUATION FOR LEAD.

ZERO OF STRESS TRANSFERRED TO 6.007 FROM 17.25. $x=x'+11.243.$

	x^3	$+.79338x^2y$	$+.204076y^2x$	$+.0175276y^3$	$-12.268x^2$	$-6.3458xy$	$-.8358y^2$	$+48.825x$	$+13.18y$	$-66.33=0.$	
$x=6.00$ $y=0.$	216.76				—442.68			+293.29		—66.33=0.	510.05 — 509.01
$x=3.00$ $y=2.20$ } 1	27.	+15.709	+2.963	+ .1866	—110.41	—41.882	—4.045	+146.47	+28.996	—66.33 =0.	221.3 — 222.6
$x=2.88$ $y=1.7$ } 2	23.88	+11.18	+1.69	+ .0861	—101.75	—31.06	—2.415	+140.6	+22.405	—66.33=0.	199.83 — 201.52
$x=0.91$ $y=3.8$ } 3	0.75	+ 2.496	+2.681	+0.96	— 10.159	—21.94	—12.06	+44.43	+50.08	—66.33=0.	101.39 — 110.49

Test 1. Die Hütte, p. 236. Tests 2 and 3. Prof. Dewar.

$X@$	$Y@$		Summations.	
		MUNTZ-METAL.		
16.00	—2.74		13214.42	13185.55
2.99	33.6		7674.42	7670.18
4.7844	20.5		8356.13	8357.46
4.507	38.25		10483.7	10484.02
		SILVER.		
13.335	—2.74		7310.94	7311.4
2.73	28.33		4328.05	4325.78
3.73	23.27		4131.5	4129.05
4.73	18.58		3996.04	3992.63
		TIN.		
3.00	3.5		171.725	172.834
2.88	4.5		182.91	183.17
0.91	8.7		125.50	124.23
		ZINC.		
3.00	5.26		406.48	406.408
0.00	19.03		490.22	492.8
		BISMUTH.		
3.00	2.2496		174.77	176.56
2.88	1.3		148.35	150.45
0.91	0.67		40.176	54.09
		LEAD.		
3.00	2.20		221.32	222.66
2.88	1.70		199.83	201.52
0.91	3.8		101.39	110.49

by the nine given points or pairs of coördinates, determining the curve.

On this account the latter are said to determine the locus of the curve and are forced to indicate the individuality of each kind of matter as expressed by the relations of the ordinates determined experimentally.

The peculiarity alluded to can be seen readily upon our Chart A. It occurs between the stations $X = 2.74$ and $X = 4.23$ in the curve for iron.

There is no indication contained in the values of X and Y, for these stations, that a sudden change must occur in the interval thus defined.

Nevertheless, the locus, as expressed by the nine pairs of ordinates, determines towards $X = 3.74$ first a rise and then a fall in the values of Y that must have escaped the attention of the experimenters.

In fact there is no way for them to detect the change unless they had happened to make a test in that interval.

Our Chart A shows this bulge, in dotted lines, as indicated by our equation and as given on Table IV.

The importance of this result is realized when we compare our curve with those shown on Chart I, where similar curves, based upon other experiments, are recorded.

Here similar changes are to be seen on lines 12 and 13, taken from experiments of the British Admiralty.

Also the dots taken from Styffe's results indicate that, at about these temperatures, very sudden changes of a similar character are found in the classes of irons on which he experimented. In short, we have a complete verification of the fact that, irons of a certain class possess this peculiarity.

The change must then occur from natural and internal causes that are covered in the relation of these ordinates.

If this be admitted, then as stated, we have another strong indication that our equation expresses truly the internal conditions reigning in the material.

The Individual Struggle Atom to Atom where Heat Measures Cohesion.

With the above mentioned results at hand, we are justified in extending our study for the purpose of adding to their number.

We have seen that these cubic equations, when bound to existing facts by so many sets of experimental data, express the conditions existing between the molecules in mass. It is very evident though that they can only do so correctly when the locus passes through the proper melting-point, namely, that one corresponding to the material in question, and when it crosses the abscissa under the constant condition of

$$\frac{X - M\,P}{Y} = \frac{1}{273}.$$

Later, it will be shown what this condition prescribes, though now we assume this result to follow only because it represents a known fact, recording the expansion of gases with rising temperature.

It is well known that linear expansion can be determined by taking the cube root of the volumnar.

We can do the same here, but it would mean something more, for we would assume conditions to be such that expansion in one direction alone was measured.

This difference might be expressed by a linear expansion existing between a pair of atoms, while the volumnar must take place among many, acting as a mass.

If we could extract the cube root of our equation, we would have the struggle of cohesion and heat confined to a development of energy in one direction only, when we could measure the same physical change expressed by a variation of temperature in the older equation.

The simpler equation would then have its own zero of stress at a station, or temperature, different from that of the original.

Between these two zeros corresponding to the growth of cohesion from the simpler to the complex form, when measured by heat, a definite physical change would be established by the temperatures indicated.

In the cubic equation the angle of the straight line with the abscissa when leaving the melting-point determines a constant relation between our ordinates, *i.e.*, 1/273.

Similarly, the relation of the new ordinate near this zero may be expected to indicate some constant relation and should claim our attention.

If our formula for iron and its six derivatives fulfil completely our sequence of prescribed conditions, they should also admit of our tracing this struggle of cohesion vs. heat to its source.

It will therefore be interesting to extract the cube root of these equations.

By doing so we find in the case of iron, for example:

$$X+0.2624\ Y-15.308=0.$$

for silver: $X+0.2624\ Y-10.385=0.$

On Table X the remultiplication of these roots has been undertaken to compare the resulting product with the original equation, as some slight variations exist.

This product is called the new equation on the sheet where the old and the new equations for these metals are shown in juxtaposition for the purpose of facilitating the comparison.

The number of terms in the formulæ, the similar signs, the most pronounced resemblances in the value of the coefficients preclude any idea that the original equation is a true cube by chance only.

At the same time the simplicity of form in the root indicates that the experimental rupture test must have expressed some simple law.

TABLE X.

$x+.2624y$	-15.308	$=0$			Comparison of old equations for iron with the cube of the new equation $(x+.2624y-15.308)^3=0$, when the basis of change is 100 deg. C. taken as a unit.				
$x+.2624y$	-15.308	$=0$							
$x^2+.2624xy$	$-15.308x$								
$.2624xy$		$+.068855y^2$	$-4.01686y$						
	$-15.308x$		$-4.01686y$	$+234.335$					
$x^2+.5248xy$	$-30.616x$	$+.068855y^2$	$-8.03372y$	$+234.335$					
$x+.2624y$	-15.308	$=0.$							
$x^3+.5248x^2y$	$-30.616x^2$	$+.068855xy^2$	$-8.03372xy$	$+234.335x$					
$.2624x^2y$		$+.13771xy^2$	$-8.03372xy$		$+.018167y^3$	$-2.10807y^2$	$+61.49y$		
	$-15.308x^2$		$-8.03372xy$	$+468.67x$		$-1.054y^2$	$+122.98y$	-3587.2	
$x^3+.7872x^2y$	$-45.924x^2$	$+.206565xy^2$	$-24.11116xy$	$+703.005x$	$+.018067y^3$	$-3.16207y^2$	$+184.47y$	$-3587.2=0.$	New equation
$x^3+.79338x^2y$	$-45.997x^2$	$+.20476xy^2$	$-24.1858xy$	$+703.9x$	$+.017526y^3$	$-3.1302y^2$	$+184.817y$	$-3587.2=0.$	Old equation.
$x+.2624y$	-10.385	$=0.$			Comparison of old equation for silver with the cube of the new equation $(x+.2624y-10.385)^3=0$, when the basis of change is 100 deg. C. taken as a unit.				
$x+.2624y$	-10.385	$=0.$							
$x^2+.2624xy$	$-10.385x$								
$+.2624xy$		$+.068855y^2$	$-2.7250y$						
	$-10.385x$		$-2.7250y$	$+107.848$					
$x^2+.5248xy$	$-20.77x$	$+.068855y^2$	$-5.450y$	$+107.848$					
$x+.2624y$	-10.385								
$x^3+.5248x^2y$	$-20.77x^2$	$+.068855xy^2$	$-5.450xy$	$+107.848x$					
$+.2624x^2y$		$+.13779xy^2$	$-5.450xy$		$+.018067y^3$	$-1.4301y^2$	$+28.28y$		
	$-10.385x^2$		$-5.450xy$	$+215.69x$		$-.7150y^2$	$+56.56y$	-1120	
$x^3+.7872x^2y$	$-31.155x^2$	$+.206565xy^2$	$-16.35xy$	$+323.538x$	$+.018067y^3$	$-2.1451y^2$	$+84.84y$	$-1120.\quad=0.$	New equation
$x^3+.7933x^2y$	$-31.252x^2$	$+.204076xy^2$	$-16.3869xy$	$+324.221x$	$+.0175276y^3$	$-2.1217y^2$	$+85.105y$	$-1119.96=0.$	Old equation.

It is proposed to accept these roots provisionally, as well as the new cubic equations as corrections of the older ones.*

Before explaining the use of these equations it is desired to change their form both in order to alter the original period, or the temperature unit, and to change the designation of the ordinate from Y to Z.

This is desirable in order to prevent confusion between the determination of the equations of the third and of the first degree.

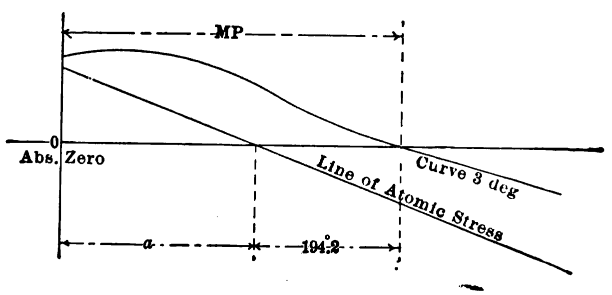
As the original temperature unit represents 100° absolute centigrade, and as it is now proposed to return to the ordinary absolute degree, our values in relation to X must be multiplied by one hundred.

Introducing these changes our formulæ become:

$$X + 26.24\,Z - 1530.8 = 0.$$
$$X + 26.24\,Z - 1038.5 = 0.$$

wherein Z refers to determinations expressing reactions between pairs of atoms only.

Returning then to the common form of these equations, it is evident that they represent conditions of physical change of the simplest character. As is well known this style of formula represents a straight line intersecting its abscissa, as shown



in the sketch where, with increasing values of X, Z equals zero. By calculations from either of these equations of various values of Z by assuming values of X, we find $+Z$ a maximum at absolute zero decreasing proportionately with the temperature

* On Tables VIII and IX it was seen that at low temperatures the equality of the summations was less correct than when the numbers were higher; by the acceptance of this true cube these irregularities must disappear.

changes, until Z equals zero, whence $-Z$ increases indefinitely, while the calculated values all fall in a straight line.

Introducing the values of $Z = 0$ in our two equations, we have, for iron $X = 1530.8$
for silver $X = 1038.5$
while the melting-point for iron is 1725 and for silver 1233.5.

The intervals then found between the two zeros are:

$$1725^\circ - 1530.8^\circ = 194.2^\circ$$
$$1233.5^\circ - 1038.5^\circ = 195^\circ.$$

We have then a constant interval of physical change of 194.2° during which the energy of heat must measure that of cohesion while undergoing the change from the atomic to the molecular condition.

It must be understood that this value of 194.2° is a constant because, in the transfer of the cubic equations from one melting-point to another by the substitution of $X'+b$ for X, the choice for the term b was made under the condition that the gaseous expansion should be constant, and as near 1/273 per degree as the formula could make it.

The balance of our six equations yield a similar result.

We can then assume, hypothetically, that this new zero of atomic stress always falls at 194.2° below $M\ P$ and that if we desire to write the equation, of the first degree, of any material, it is only necessary to find the third term, the first two being common to all. Lastly, in order to find the third term we have only to deduct 194.2° from the melting-point.

Our equation then assumes a common form.

$$X + 26.24\, Z - a = 0.$$

in which a equals $M\ P - 194.2^\circ$ and X represents the number of degrees centigrade separating our station from absolute zero.

As stated, the constancy of this interval in these formulæ is due to the application thereto of the equality of the ratio $\frac{T}{-Y}$ representing the equal expansion of all gases at the rate of 1/273 per degree centigrade.

This application was tested by shifting the origin of the gaseous expansion from the melting-point of iron to those of six other metals. It probably applies to other systems, as well.

We were certainly able to prove the accuracy of this assump-

tion by the adaptation of the six equations to the solution of seventeen individual cases under experimental test values.

In each case the equality of the positive and negative summations testified to the accuracy of the adaptation.

Instead of shifting the origin, however, we can, as now seen, deduct the constant 194.2 from $M\ P$, and cube the simple formula of the first degree.

Thus we can readily obtain similar corrected equations of any desired body which could be charted as shown on Chart D.

Referring once more to the comparison of seventeen sets of calculated and experimental rupture tests we have derived from the formula of iron, it is clear that the internal changes, covered by our methods, are distinctly related to each other, even if occurring in six different metals at various temperatures.

In other words the relations existing between the various rupture curves of different metals, under change, can be distinctly brought out. As indicated graphically upon Chart D, we have the means of constructing a universal chart. For the struggle between cohesion and heat, while varying for each individual adaptation, evidently obeys a general law.

We have seen that the breaking stresses of each solid can be determined for each temperature, and as the lines below the abscissa are straight and parallel in all cases, the curves can be developed in the upper as well as in the lower quadrant.

The correct representation of the many experimental situations results: (1) because the common relations of our ordinates, conveying the law, are correctly expressed for the conditions actually occurring within iron. (2) because this relation needs only to be correctly limited to cover other individual cases. (3) because in each case, this limit can be covered by a variable interval of change, measured along our abscissa, locating correctly certain fixed conditions or states.

These are the points of origin of the values of our ordinates, or their zeros. They are :(1) the zero of absolute temperature; (2) the zero of cohesive stress. This latter naturally falls at the melting-point which thus becomes a controlling factor in the determination, as the other zero is common to all.

Our curves of the third degree then express serial changes and determine specific loci, for each case, under gravitational law. They cover the relations between cohering molecules in

the solid state in the upper quadrant, and between movable ones in the lower, thus furnishing the data for a universal chart, as stated.

The general formula for all these intermolecular actions, when characterized by the value of the melting-point can be written:

$$(X + 26.24\ Y - (M\ P^\circ - 194.2^\circ)\ )^3 = 0$$

A second, and even simpler law, can be deduced immediately, for, by extracting the cube root of this equation, a direct and elementary relation is discovered to exist between a stress, acting in each of three directions, and these temperature changes. This stress is, however, a lineal one and not a rupture stress, or one measured by cubical bonds to all adjacent parts.

To avoid confusion we have already distinguished this new stress by the letter Z. These specific linear stresses, acting in three directions, must be interatomic in contradistinction to the cubical ones as molecular. The formula can be written:

$$X + 26.24\ Z - (M\ P^\circ - 194.2^\circ) = 0.$$

There is then reason to believe that our new law covers the changes due in this fundamental and gravitational stress which is operative between the smallest particles of matter, when under change by heat.

By its form the formula shows that this interatomic stress must vary directly with the absolute temperature, or at a constant rate per degree of change. It meets its zero at another station however, and this new point can also be utilized to distinguish between developments of physical or chemical energy.

From the equation we see that this stress must have both positive and negative values, in each body, depending upon the choice of stations above and below the zero value.

Each kind then, when developed through a volume of change or a suitable temperature interval, must, like the opening or closing spring, develop energies of different varieties.

In order to test these points it will be shown how the determinations of the formulæ can be applied to calculations of various amounts of energy, spent or collected by matter, under certain elementary changes in volume.

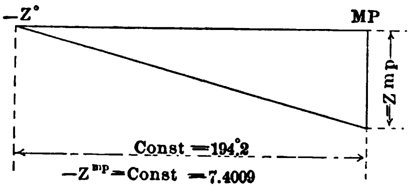
As regards the changes in stress value, and owing to the constant interval lying between the zero of atomic stress and

the melting-point (194.2°) the value of the atomic stress at the latter station is also constant.

From the last equation, when X represents $M\,P$ we have:

$$Z^{mp} = \frac{M\,P^{\circ} - 194.2^{\circ} - M\,P^{\circ}}{26.24} = -\frac{194.2^{\circ}}{26.24} = -7.4009$$

The question arises then: Can this atomic stress or pressure $-Z$ be identified with the osmotic pressure, which also varies directly with the absolute temperature, is controlled by the



mass action (cohesion) and shows equal pressure in solutions having the same freezing-point and the same solvent, as proved by van't Hoff?

The Energy of Atomic Pressure.

The Producer of Physical Change.

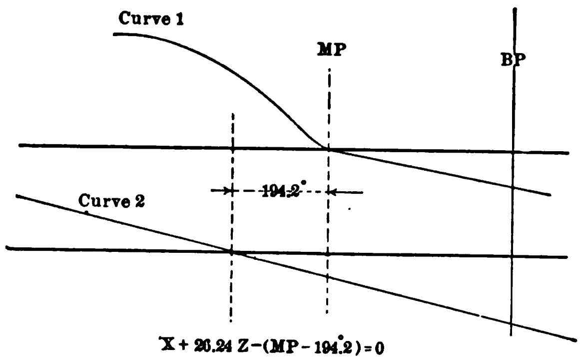
In calculations of the development of energy by the expansion of steam, one figures upon the utilization of a certain average pressure within a given cylinder, having a known diameter and length. These factors determine an actual working volume through which this average pressure is exerted.

The development of energy thus described is an example taken from material in the molecular condition, because it results from gaseous pressure. On the other hand it will be shown that chemical energy is developed from atomic pressure, when developed through the chemical volume.

This chemical volume is one resulting from expansion of matter by heat against cohesion, or vice versa of contraction upon cooling, between two stations or temperatures.

It is thus a measure of physical change, in that it determines the energy freed by heat or bound by cohesion in the volume covered between said stations, under specific changes of the atomic pressure. These physical changes are then a transformation of matter with a simultaneous change of energy bound by cohesion.

When we turn to investigate this question, we note that in addition to our curve of the rupture tests, which is represented by curve 1 on the adjoining chart, we can now construct a



second one from our formula of the first degree. This is marked No. 2 on the chart and is descriptive of the law determining the growth of the counterstress Z when it varies with the changing temperature.

The two curves are so placed that their melting-points correspond. It can readily be seen that while the zero, or the intersection with the abscissa, falls at the melting-point in curve No. 1, that of No. 2 occurs at $M\ P^\circ - 194.2^\circ$.

As the former curve expresses the change under cubic expansion, and gives the rate of change of volume, we realize that in passing through zero, a change in the rate of development of this factor of our energy calculations must have occurred.

Therefore while some period of change must finish here, another must originate to be developed under higher temperatures.

The latter curve through its zero indicates the origin of the negative stress. The former with its zero at the melting-point determines the origin of the gaseous volume.

Two intervals of change are thus determined.

1st. That one where the negative stress $-Z$ is developed through a period of 194.2° of change to the melting-point.

2d. The development of the same stress through any number of degrees of change originating from the melting-point.

It will be shown that the energy of heat developed through this period of 194.2°, where the cohesion of the solid is overcome, represents a unit of the energy developed by solution.

It will also be shown that the energy of heat developed beyond the melting-point can be determined to any specific station, but under certain conditions the result determines also the chemical energy of the unit mass of the material represented upon the chart.

This second question will be considered first because in this manner we can the more readily reach greater numbers of experimental values for comparison with our calculated ones.

Development of Chemical Energy.

The first point to claim our attention is the situation found at $M\ P^{\circ} - 194.2^{\circ}$.

According to the statement above we should expect to find the material at this station possessed of both its heats of solution and its chemical energy.

In regard to this view of the case we have as confirmatory evidence the fact that, even in periodic form, the atomic volumes (solid) represent the amounts of energy possessed by the various elements. Our view would then simply suggest that the most accurate temperatures for the determination of the specific gravities might lie at $M\ P^{\circ} - 194.2^{\circ}$ for then the records would be comparable.

Again we have the fact that the internal constitutions of solutions known as " normal " contain the full chemical energy of that certain equivalent u of the molecular weight it is chosen to represent. It is in the fluid condition and therefore corresponds with that which is found at our station $M\ P$.

This general situation recalls that of the atomic volume (fluid) for this also represents $\frac{u \text{ gram equivalent}}{\text{One vol. solution}}$ where u represents any chosen multiple.

If our theory can be proven, we should expect then to find the chemical energy to be represented by the development through heat of any remnant of cohesion from the fluid state to the boiling-point under atmospheric pressure, or of all internal energy to that station. Having reached this point it would simply be a question of the comparison of the results of our methods with experimental ones. If the comparison were favorable in a sufficient number of cases, the question could be considered as proven.

The Unit Mass.

All generalizations regarding the development of chemical energy unite in defining a specific mass for each body, as the base of all chemical combination, under multiple law. Hence the term Unit Mass. It is the agent to which we must trace all chemical energy which results from combinations of these units.

It is that unit mass therefore of each body that is able to cleave together, to act independently, being bound by the cohesion of its parts in the solid state. These parts are however sometimes drawn to foreign bodies, by the same force forming compound molecules.

It is the energy of this mass, both in the fluid and solid, which we seek to define by a determination of the amount of heat energy required to bring the mass to certain temperatures or stations against the internal cohesion supplemented by the resistance of the external atmosphere.

We will now attempt a description of what is meant by the term " Unit Mass," which we must call the atom.

The reader must distinguish between the new meaning applied to this term and the one ordinarily received.

It is not an indivisible unit but must be conceived as consisting of innumerable particles, each pulsating at a specific rate according to the station its temperature occupies above absolute zero.

It is evident, however, that each of the above mentioned particles forming a unit mass must, in varied extent, attract every other one present. Then the action ensuing can be summed as the reaction of one half mass against its neighboring half mass, making the half mass the acting unit of cohesion within the unit mass. At the same time the " Chemical Unit Mass " may often consist of one, two or more such unit masses, each of which, however, will contribute similar amounts of cohesive energy towards a grand total.

The Unit Measure.

It has been proved that the general chemical properties of the elements vary periodically with the increasing values of the atomic weights. Among these properties may be mentioned the power of forming oxides and chlorides of definite composition.

This power must be considered as a demonstration of the amount of chemical energy possessed by the chemical unit mass acting.

The atomic volumes also vary under similar periods. This fact is distinctly shown in the periodic curve of the atomic volumes.

On this account it is generally recognized that the atomic volumes solid is a unit measure of the amount of energy contained in matter.

Each atomic volume, however, represents an independent state for each body at some fixed temperature. The chemical energy still held by the mass must be that retained at that temperature.

Its condition is expressed by the ratio $\frac{\text{Atomic Weight}}{\text{Specific Gravity}}$.

Each value forming this record, however, represents a specific case of $\frac{\text{Unit Chem. Mass}}{\text{Mass per unit Vol.}}$.

It is thus literally the number of volumes holding the unit mass on a scale determined by the volume of the unit weight of water at some fixed temperature.

It is however the contemporaneous change within the latter unit mass and unit volume that determines the rate of internal energy change in degrees and calories.

On this account, and under the generalization given, we must expect the energy of internal change to be measured in commensurable units. For, while the energy of the unit mass (chemical energy) acts directly under cohesion in one sense, that of heat, on the other, acts upon the volume by expansion. And, as the corresponding developments of the two methods are equal at every change, and are, in each case, measured in similar volumes, degrees and calories, they will be expressed in commensurable units.

Then, under the generalization above mentioned, the internal energy of the atomic volume is also a constant, if the stations are correctly chosen. This unit is capable of measuring the internal condition of any material, for an atomic volume of two or three must carry two or three times as much energy as a single unit volume. Then the chemical energy of any mass can

be expressed by the product of the number of atomic volumes present into the amount of energy held by one atomic volume.

Other chemical results confirm this view, for a somewhat similar rule applies when the unit mass goes into solution.

As is well known the normal solution, holding the equivalent in a given volume, carries the full chemical power of the material. Its internal energy can be divided according to the number of volumes used.

Among gases also the combining volumes bear fixed relations to each other, so that their respective energies under cohesion are measured by the internal changes of certain volumes under standard conditions.

Each of these states, the solid, the liquid and the gaseous must represent a fixed station in the struggle of cohesion and heat, for each qualifies some specific distance reigning between their atom centers, by the number of volumes described.

In each of these states the reigning temperature must have developed a fixed amount of energy of heat from a common point of origin, the absolute zero. This energy must equal that of the cohesion overcome, while that remaining must be the chemical energy still held.

Hence it was decided that while the atomic volumes solid is recognized as a theoretical unit for our purposes, some other unit of a similar character could be chosen to measure the energy of the unit mass if for any practical reason it should be preferred to the solid one.

Owing to the porosity of matter, however, the positive determination of a constant specific gravity of the solid becomes difficult.

Hence the atomic volume solid can only approximate the true situation we wish to cover and a better one must be sought.

A Similar Unit.

Our methods scored an advance when in the exploitation of our equation of the third degree, we utilized the fact that all gases expand equally. In like manner it is desired to make use of another generalization.

This latter may be stated as a result obtained experimentally by Regnault with diatomic gases. It is described as follows in Barker's Physics, p. 286:

"He (Regnault) concludes: 1st, that for approximately perfect gases, the specific heat does not vary with the temperature; 2d, that the thermal capacity of the unit mass is independent of the pressure or density of the gas, and hence that the thermal capacity per unit volume varies as its density; 3d, that the thermal capacities of equal volumes are equal for the simple and more difficult condensible gases, and also for compound gases formed without condensation; and 4th, that for easily condensible gases these laws do not hold; the specific heat, for example, increasing with the temperature.

Our new departure can then be stated as follows: Atomic volumes may measure the energy of the unit mass at a given rate per volume from a fixed station. While however this determination may be sufficiently accurate to impress its results upon us as a general principle it can only be as an approximation to more correct values. For, owing to variations in specific gravity it is difficult to obtain correct atomic volumes. The solids obtainable for experimental purposes are never of equal texture throughout, all being more or less porous locally.

Hence this method of determining individual amounts of energy must be recognized as approximate.

Paragraph three, as given above, describes a more suitable unit.

It states that the "thermal capacities of equal volumes of gases are equal" under certain prescribed conditions.

Hence these equal volumes and their equal thermal capacity can form our new unit, provided we can arrange that the prescribed conditions are met, *i.e.*, that all loss by condensation can be prevented either from latent or from sensible sources.

Under clause 2, we see that the thermal capacity of the unit mass is independent of the pressure and density of the gas and hence its thermal capacity per unit of volume varies with its density.

This variation of the density per unit volume when representing the unit mass in various bodies can be expressed, however, by the unit n covering the number of volumes holding this mass, each of which, however, is subject to physical change simultaneously.

We have thus partly defined a new unit of measurement somewhat similar to the atomic volume, but more accurate in character.

But, as stated, these equal volumes with their measured thermal capacities are of equal value, and on that account are results of equal physical change. In their formation, or by their expansion they measure the simultaneous development of the energy of cohesion of the unit mass when overcome by that of heat under equal units of change per part n thereof.

Like the atomic volumes then these volumes of expansion may measure the energy of cohesion of the solid or liquid from some selected station, or temperature, to a certain final station near the boiling-point, where the last trace of internal energy must be overcome by the expenditure of the latent heat of vaporization.

Then the change could be measured at the rate of 273 degrees per volume, as a unit of expansion against the energy of the mass or of the atmosphere. But just as the mass must be looked upon as the acting mass unit, so must the amount of physical change be reckoned in units of volume and not in degrees.

Hence the effort to trace the relation of one volume of change by expansion, when it represents some aliquot part of the unit mass, for it also must be a commensurable unit limiting change as well as the atomic volume.

Reverting to this latter unit, let us suppose the unit mass, in gas form, divided at some fixed station near the boiling point, into s volumes. Then the weight held in each volume will be $\frac{\text{Mass}}{s}$. But the weight of one volume is the specific gravity of the same at the stated temperature. Hence the relation of one of these volumes to the general mass unit will be $\frac{\text{Mass}}{\text{Sp. G.}}$

Now the generalization that the energy of the unit mass can be expressed in the number of atomic volumes must mean that the cohesive energy of the unit mass, at a fixed station, is equal to the heat energy of s volumes, and that the latter can be developed by expansion, when this unit mass is subject to change from some initial station. Then at this initial station we must have

$$\text{Energy unit mass} = \text{Energy } s \text{ Volumes, or}$$

$$\frac{\text{Energy unit mass}}{\text{Energy } s \text{ atm. vols.}} = 1.$$

If we change this divisor to unity, however, we have the expression for which a similar unit is to be sought, as:

$$\frac{\text{Energy unit mass}}{\text{Energy 1 atm. vol.}} = \frac{s}{1} = s.$$

The Unit Volume of Expansion.

In our struggle of cohesion vs. heat we must then select our own methods of expressing how the energy of the unit mass can be measured by another internal agent whose developments are convertible from degrees into volumes of expansion, thus measuring specific changes towards a total which can be represented by n volumes.

This equal thermal capacity of equal volumes of gas under fixed conditions presents one capable of universal use, when a unit expansion of 273 degrees is adopted.

Let us endeavor to sketch hypothetically a condition that eventually shall produce an equivalent position at the same final station, when the unit mass is held in n volumes and when all loss of energy is guarded against. When it is sought to limit a period for the development of chemical energy we have to determine the proper initial station. This latter may vary, however, for we may or may not desire to include the heats of solution. Thus two cases are possible. But it should always be understood that in the calculation of chemical energy the energy of the solid during solution is excluded. We can however, qualify the situation still farther.

For this purpose let it be understood that the conditions to be described apply only to those found among the elements and formed compound bodies. In these cases, the two half atoms in presence of each other are similar in every respect, in contradistinction to those cases where the atoms are in the act of being formed from unlike particles. At this moment we can understand that when the two parts acting by cohesion are of unequal mass, as in the act of combining chemically, variations in the value, or relation of each unit to its neighbor, must occur, causing changes of volume.

Under these conditions let us suppose a unit mass to be situated at the melting-point, as an initial station, exposed to a rising temperature until the same final temperature is reached near the boiling-point.

We thus expand our unit mass into *n* volumes of 273 degrees each overcoming all cohesion under atmospheric conditions, until complete gasification ensues. At this station the latent heat of vaporization has been supplied to the unit mass, and as stated, gasification is complete.

We thus replace the unit atomic volume by another unit measure of cohesion, but one that can be, in its turn, measured by the heat energy, in accordance with the general purposes we have in view. Thus the unit volume determined by an expansion of 273° becomes a measure of the energy of cohesion of the unit mass, just as happens in the case of the unit atomic volume.

Then the situation can be expressed, somewhat as before, by Energy unit mass = Energy *n* vols expansion, or

$\frac{\text{Energy unit mass}}{\text{Energy } n \text{ Vol. exp.}} = 1.$ Reverting to the unit volume of expansion, we have:

$$\frac{\text{Energy unit mass}}{\text{Energy 1 vol. exp.}} = \frac{n}{1} = n.$$

Under the conditions stated then, this latter unit value is affected equally by every physical change of 273° in the $\frac{\text{unit mass}}{n}$ in the gaseous condition originating at the melting-point, because the thermal capacities of gases are equal when these latter are possessed of their latent heats of vaporization or before any condensation can arise.

This unit can be abbreviated to $\frac{\text{Mass}}{n \text{ Vols.}}$, but when the energy of several equivalent weights *m* of the unit mass are to be covered, the situation can be expressed as

$$\frac{m}{n} \times \frac{\text{Mass}}{\text{Vols.}}$$

This term is then intended to express the fact that the expansion through *n* volumes of change of 273° must equal the energy covered by *m* units of mass of a certain material to and from the stations mentioned.

If this definition of the unit measures of energy can be accepted, the calculation of the chemical energy will be resolved into the determination of the product of these certain volumes into the proper stresses.

THE CHEMICAL VOLUME.

This volume of change which we must endeavor to define more closely, can be called the "chemical" when limited to the expansion lying between an initial and some other final temperature. It can be expressed by the number of degrees found between these stations in its relation to 273 as the unit of one volume of gaseous expansion. This quotient can then be called the strain of volume.

THE MAXIMUM CHEMICAL VOLUME.

By this term we can specify that chemical volume in which the energy of the unit mass is developed by heat against cohesion under atmospheric pressure. On this account it measures the amount of energy of cohesion possessed by the unit mass under natural conditions of density at a fixed initial station whence the amount so held can be measured by expansion to a final station.

It is then the volume in which the change of stress occurs under a specified change of temperature, and when the average stress develops energy pro rata in accordance with the values of these factors.

The maximum chemical volume then is intended to express the specific amount of expansion which develops that portion of the molecular energy of the unit mass which is converted into chemical energy and which must be developed between predetermined stations, under 760 mm. pressure.

It is then this maximum chemical volume that interests us in the determination of chemical energy.

THE INITIAL STATION.

For such determinations we must locate our initial station at the zero of stress.

If, however, we wish to eliminate the energy known as the heat of solution, we must disregard the volume of expansion met with under negative atomic stress before the melting-point is reached.

Then the initial station for volume, under the present conditions, will fall at the melting-point and it will represent the origin of the maximum chemical volume.

It thus coincides with the origin of the gaseous volume, for we shall see later that the chemical energy proper is caused

entirely by the energy developed in the gaseous condition, and which can be measured, as suggested, by n expansions of the gaseous volume at the rate of 273° per volume.

Under these circumstances the condition of the material at the initial station $M P$ corresponds to a certain extent with that of the normal solution, where the unit mass u can be held in n volumes, and while the chemist uses the solution volumetrically for the determination of the chemical energy, we, on our part, utilize the number of volumes of expansion to a final station to measure the amount held at the initial station, where the mass, as stated, is also in the fluid state.

On this account we must determine the number of volumes of expansion submitted to before reaching the final station, bearing in mind that each interval of 273° of change represents one expansion undergone by the unit mass, or by the two half atoms reacting.

There seems then to be a certain similarity between the two methods, and if it can be shown that the results are fairly similar in a number of cases, our methods must receive support.

The Final Station.

In order to measure the energy of cohesion for the maximum chemical volume of the liquid under atmospheric pressure, it is evident that we must locate not only the temperature at which matter vaporizes at the boiling-point, but some station near that point, where the latent heat of vaporization has been supplied under 760 mm. pressure.

The term maximum chemical volume is meant to specify the amount of expansion from the melting-point to that final station where the gasification of the unit mass is complete, under 760 mm., or after the latent heat of vaporization has been supplied when taken relatively to that of one volume of expansion.

It can be rendered as follows:

$\frac{\text{Final station}^\circ - M P^\circ}{273^\circ} = n$ Volumes, where each volume represents the heat energy developed by a change of 273°.

Chemical Energy.

For the present we must indicate the stress occurring at our final station as that found at the boiling-point, a fact that can

be explained later. Then the average stress from our initial station to that point can be written $Z^{bp}/2$.

Hence the energy developed between the named initial and final stations equals $\frac{Z^{bp}}{2} \times \frac{\text{Final St}^\circ - M\, P^\circ}{273^\circ}$.

This subject is roughly indicated upon chart E.

STUDY OF STRESS AND VOLUME BY GROUPS.

On chart *E* are shown the lines of atomic stress and the volumes of expansion for several elements. The former are calculated from our equation of the first degree, the latter are indicated by periods of 273° originating at *M P*.

They are located in groups, in one sense a recognized method of classification of the elements under periodic law, as distinguished from the various series identified by a similar classification in another sense.

Upon each chart the attempt has been made to distinguish a certain relation to a fixed volume of expansion submitted to in reaching a standard condition, which we have described as the maximum chemical volume, at that station.

Under our recent decision, we place the origin of the gaseous expansion, as well as the origin of chemical energy at the melting-point, with equal intervals of growth both in volume and in energy. Periods of 273° are noted upon the chart as indicating certain stations where the expansion must be complete to a certain stage relatively to the total cohesion of the mass, under atmospheric pressure. At intervening points, however, the growth must be fractional and the resulting density locally unequal, as in the vaporous condition where liquid is found at the circumference of the vesicular sphere only.

The above mentioned periods of 273° are carried out upon the chart until the neighborhood of the boiling-point is reached.

The last point chosen is marked V^v to represent our final station of the maximum chemical volume, which falls either just inside or outside of that station.

The periods vary in number from one to four, and show various relations to the different groups.*

Our chart indicates that the motion causing the atomic pressure $-Z$, while overcoming any balance of cohesion under

*These relations are fully described later.

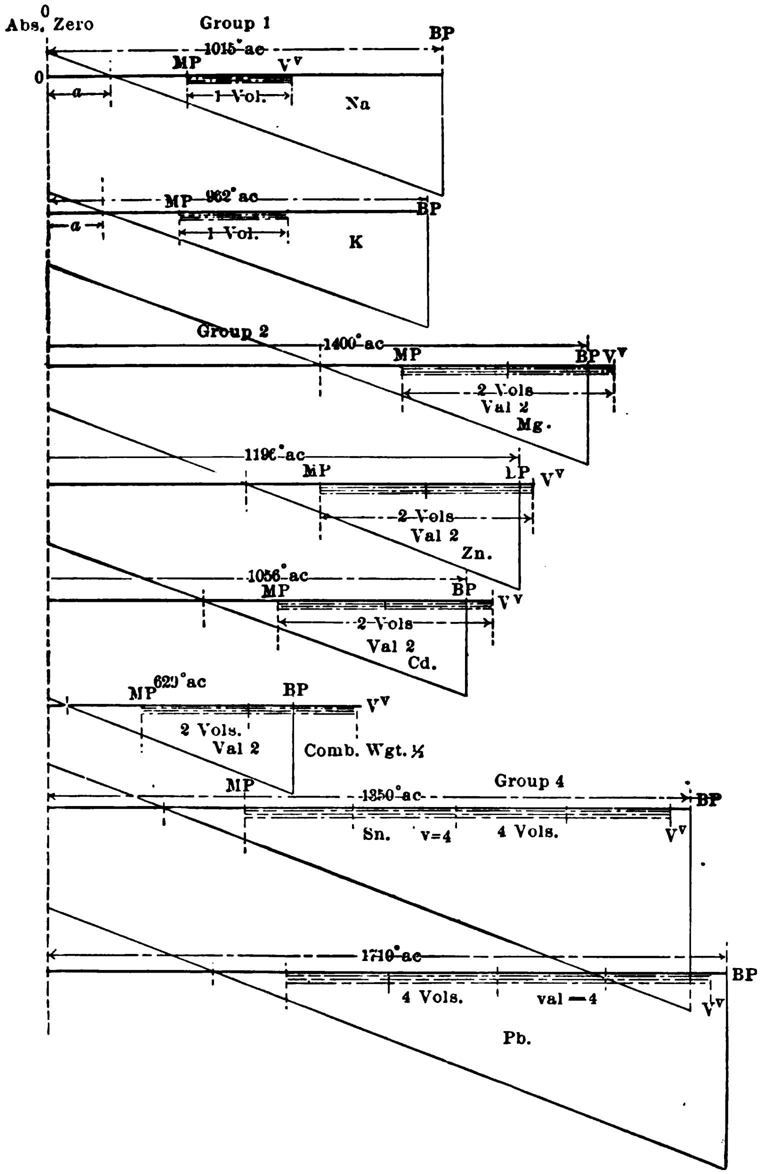


CHART E.—Study of Stress and Volume by Groups.

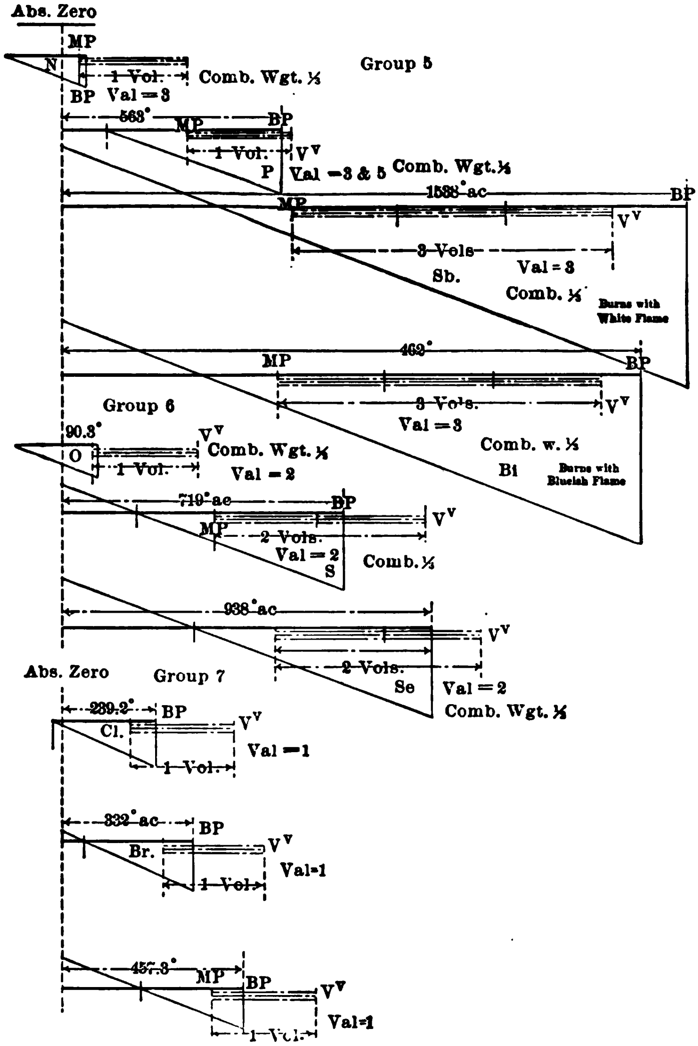


CHART E.—Study of Stress and Volume by Groups (Continued).

atmospheric pressure, varies greatly at the different boiling-points in different groups. But in a general way, the reacting pressure is constant, and these variations must be caused by the internal conditions governing cohesion.

Let us fix our attention upon the cases where the station V^{v} falls beyond the boiling-point.

At the latter point some inequality of expansion must evidently be present among the particles forming the mass in the chemical volume. Some balance of energy is required. This balance of energy corresponds to that necessary to complete the measure of expansion as determined by the position of V^{v}.

It will be demonstrated that the latent heat of vaporization is the amount required to bring the specific unit mass to this complete volume of expansion, or to the limit of the chemical volume as expressed by $\frac{\text{Mass}}{\text{Vol.}} = 1$, or $\frac{\text{Mass}}{\text{Vol.}} = \frac{1}{2}$ etc., as the case may be.

Evidently at the boiling-point the internal atomic stress has reached the limit of the reacting pressure, or of the atmospheric pressure and therefore the temperature cannot rise higher.

If more energy is required to equal that of the mass held, a further expansion without change of temperature must take place.

If this condition can be proven it is evident that the completed, or standard, condition of $\frac{\text{Mass}}{\text{Vol.}}$ covering our struggle, and which is due as the final station of the chemical volume will fall at V^{v}.

Then at last the heat energy of the system must balance both the cohesion of the solid and of the liquid states.

At this station we must also have the origin of the perfect gaseous state, as, by the above mentioned means, all latent heat has been supplied, and in consequence the specific heat ceases to vary with the temperature.

Even the relatively slight atomic energy of the liquid state reacting against any balance of atmospheric pressure has disappeared or reached zero having been replaced by heat energy. Upon cooling, however, the reverse process ensues until at absolute zero all heat energy has disappeared, while cohesion reaches its maximum.

These zeros lie then at different ends of a temperature range. Our standard chemical volume accurately defined from these stations and containing a known division of mass is found complete at V^v with its energy measured by heat, though this development originated only at the melting-point.

It is evident, however, that this station would have fallen at $B\ P$ if the external pressure had been suitably high, but the location of $B\ P$ is determined, in each case, by the existing conditions.

The energy accumulated from absolute zero to $M\ P$ is measured at another rate, that of the half atom under a period of change of 194.2 degrees, as will be shown later.

THE CALORY.

The unit of physical change.

Before undertaking the calculations of the latent heat of vaporization by the development of the atomic pressure through certain volumes of isothermal change, or by an expansion between $B\ P$ and V^v, it will be well to discuss the units in which these results will appear.

The calory has been chosen as a unit measure of the energy of heat, because it is also a similar measure of the energy of physical change developed within the material at the same time, under fixed conditions of mass and volume. It is therefore particularly adapted for our present purposes.

To define it accurately the change has been limited to one degree C. or from 4° C. to 5° C. This degree, however, is the one hundredth part of the interval found between the melting and boiling-points of water.

This interval is not strictly a natural one, for the boiling-point is a station dependent upon the atmospheric pressure, and not upon the internal conditions. Theoretically a period measured by 273 degrees of change, as a natural limit, or unit, of gaseous expansion would be preferable.

Our purpose, however, is to adapt this common unit of heat and physical change to the measure of chemical energy mathematically, as a development of limited but of established change.

With this point in view we recall that the normal solutions used for chemical purposes contain each the molecular weight

of their respective mass units distributed through a fixed volume.

They are also capable of developing in their reactions, the various amounts of chemical energy that have been measured experimentally in calories. Their interactions represent then the experimental results of chemistry generally.

If we wish to study these changes and to follow them mathematically, we must first learn to limit our units to the conditions these solutions unite in presenting.

We note that in the conditions described above, the changes submitted to by the unit mass are also controlled by those of the volume they are contained in as a unit.

The energy of the mass can be subdivided by using submultiple volumes of the solution, each of these holding its equivalent of the mass. Even the combining volumes in the gas form also bear simple relations to each other.

Then the internal energy of the mass must, in each of these sub-divisions, equal that of the energy of volume, or $\frac{\text{Energy Mass}}{\text{Energy Vols.}}$ must be a constant for each condition. The changes of the one can be measured by those of the other at every station.

Our problem then is to find suitable units to measure the internal changes by those of volume under periods of change of one degree centigrade, or similar to those for which we have experimental values in calories. As a first step towards the solution of this problem, we note that the adopted unit of the internal energy of change, the Calory, measures a degree centigrade when the mass present is one kilogram of water held in one cubic decimeter of volume as a unit. Here then the internal energy of one unit of physical change, when developed within the unit mass (1 kilo) is measured by the expansion of one decimeter of water. Thus we have a fixed relation, determining the results of change and one similar to that just described, expressed between the units measuring cohesion and the energy of heat.

One Calory then measures this internal energy of change when the kilo is the unit mass, or when the term expresses the stress attracting this mass towards the earth, as matter.

At the same time the unit volume, the cubic decimeter, undergoes one unit of volumetric expansion, commensurate

with the Calory. Therefore, we have in this state the condition expressed as $\frac{\text{Energy Mass}}{\text{Energy Vols.}} = \frac{1}{1}$ under one degree of change.

This describes for us a standard condition of measuring the energy of cohesion and prescribes our units of measure. Therefore in our formulæ we must have the energy of the unit mass expressed by kilos of attraction under change, when measured within some volume of expansion. The size of this latter must be commensurate with the cubic decimeter, determining the relation of our unit to the Calory. The millimeter was chosen as the one generally taken with high stress; our stress values read therefore in kilos per square millimeter.

In limiting the change the degree absolute centigrade was chosen in order to connect our values with an established zero. Under these conditions the energy of change, in our adopted unit of one degree and one cubic millimeter, must be the one millionth of the Calory, or the one thousandth part of the gram calory.

In our formula, however, this unit is not measured by water alone or at a fixed temperature, for it expresses a unit of change wherever developed.

With volumes thus measured and with the prescribed changes in the internal atomic pressure, in kilos per square millimeter, we should always record these units equal to $\frac{\text{calory}}{1000}$ regardless of the temperature of the operation.

If this result can be accomplished, and at the same time it can be shown that these results are closely related to the actual determinations of the latent heat of vaporization, a strong argument for the truth of these methods will be presented.

The unit $\frac{\text{calory}}{1000}$ will be called herein a Calor, and abbreviated with a C, both written with a bar, to distinguish them from the larger units.

Often the experimental result is given in small calories while the calculated results are shown in Calors. In such cases the quotient $\frac{\text{calory}}{\text{Calors}}$ should theoretically be 1000.

From its actual value the accuracy of the comparison can be readily determined. For convenience this quotient has been called the coefficient B.

* * * *

THE CALCULATION OF THE LATENT HEATS OF VAPORIZATION.

Our methods have indicated that, at times, when matter is subjected to a rising temperature, and has passed the melting-point, the full cohesion of the liquid state under atmospheric conditions, cannot be overcome by heat before the boiling-point is reached.

The latter point, being dependent upon the density of the atmosphere, is not in any way connected with the internal conditions as they exist except as an interruption to a process.

As a result the material is often found as vapor or in a condition in which the balance of cohesion present is indicated by the vesicular or fog form, in contradistinction to the perfect gas, which is without cohesion. If on the contrary the pressure were high enough to have the boiling point fall at V^v this vaporous condition could not arise.

In the calculation of the latent heats of vaporization let n be the number of parts requiring vaporization. It thus expresses the number of combining volumes occupied by a gas, each requiring an equal amount of energy. In compound bodies this number is usually twice that occupied by one volume of hydrogen gas.

Let V^v, the volume at vaporization, be situated at $M\ P+273\ n$ and let it represent the final station, while $B\ P$ is the initial one. Then $\frac{-Z^{bp}}{2}$ gives the average pressure at $B\ P$ and for the volume containing the atomic mass at V^v we have:

Energy (per milligram molecule) equals

$$\frac{M\ P^\circ + 273^\circ\ n - B\ P^\circ}{273^\circ} \times -\frac{Z^{bp}}{2}\ \epsilon.$$

This represents then the energy of the full mass (cohesion) when developed by heat and when the station V^v falls above the boiling-point.

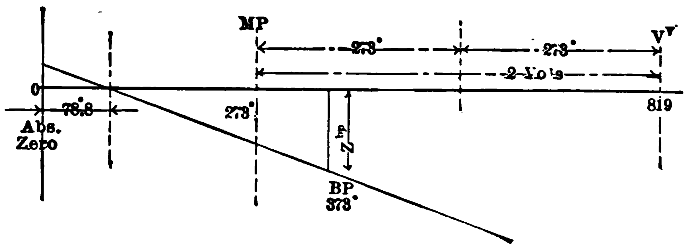
But we have this energy expressed by experimental results

for the gram molecule as: Molec. Wgt. $\times$ L. H. of V. (calories).

Then Coef. B $= \dfrac{\text{calories}}{\text{Ealors}} = \dfrac{\text{Molec. Wgt.} \times \text{L. H. of V.}}{\dfrac{-Z^{bp}}{2} \times \dfrac{\text{M.P.}^\circ + 273\, n^\circ - B\, P^\circ}{273^\circ}}$ and

$\dfrac{1000 \text{ Ealors}}{\text{Mol. weight}}$ = the formula value of L. H. of V.

Let us, for instance, take the sketch giving the details of the internal condition of water. We can see here the relations



of the various stations or temperatures.

The water will require heating to M P° + 2 $\times$ 273° = 819° = V^v before all traces of cohesion can disappear.

Thus an expansion of two parts is provided for, and while ordinarily the vapor passes off at 373° a–c, a further expansion of 819° − 373° would be required to complete the system.

Our final station falls at 819° and the initial one at 373°.

Throughout this interval of 446° the atomic pressure can rise no higher than the external resistance, *i.e.*, the atmospheric pressure. Then $\dfrac{-Z^{bp}}{2}$ develops through the new volume described.

In this case the result is 9.158 Ealors.

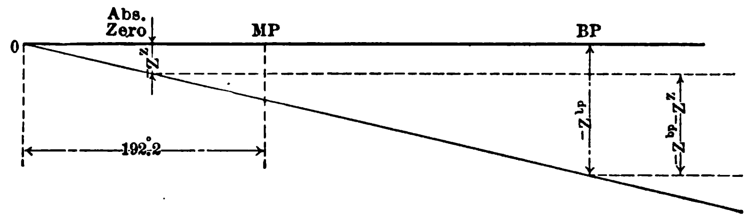
The molecular weight of water is 17.96 and the latent heat of vaporization 535.9 cals. per gram, the product giving 9624 cals. per gram molecule.

Then Coef. B $= \dfrac{9624}{9.158} = 1051 = 105.1\%$, or if 9.158 Ealors are the equivalent of 9158 cals. then $\dfrac{9158}{17.96} = 510.5$ cals., as the formula value.

On Tables Nos. XI, XII, XIII, XIV, these calculations and those for several others are worked out in detail. A compara-

tive table of calculated and experimental results is also given. The last two calculations, namely, those of carbon disulphide and alcohol will require some additional explanation.

In each of these cases the internal stress, as represented by the value of the melting-point, embodies another condition which causes slight variation in the value of the term $\frac{-Z^{bp}}{2}$ as used in the formula. This same variation occurs frequently in the calculations of the heats of formation and becomes of importance, as it relates to the whole class of materials having low melting-points. Its adaptation to this new situation is such that it confirms the value of the exhibit rather than other-



wise. The variation is found when the melting-point becomes so low that the zero of stress, marked O on the adjoining sketch, falls beyond the absolute zero.

As heat, as a mode of motion, originates at absolute zero, its energy can develop only under temperatures originating at that station. Hence the whole atomic pressure cannot be operative as calculated and a correction is necessary. The value of $-Z$ found at absolute zero must be deducted. This can be indicated by $-Z^z$. The acting pressure then is only that shown on the sketch as $\frac{Z^{bp}-Z^z}{2}$. We can distinguish this average pressure as that of class B while that of class A remains $\frac{Z^{bp}}{2}$.

By this method the calculated results of class B approximate the actual experimental ones.

In other words, the acting pressure due to the motion of heat is only that which can be accumulated from the absolute zero upwards and indicates that this zero is the true origin of motion. Other changes in the same direction and still confirmatory of this view, will be given later but this variation

from the general rule covers the situation which we are discussing at present.

* * * *

TABLE XI.

APPROXIMATION OF THE LATENT HEATS OF VAPORIZATION.

General description.

The initial condition is found at the boiling-point. The final one at $M\,P + 273 \times \text{Val.}$ and the interval between these stations $M\,P + 273 \times \text{Val.} - B\,P$.

The strain of volume equals $\dfrac{M\,P + 273 \times \text{Val} - B\,P}{273}$

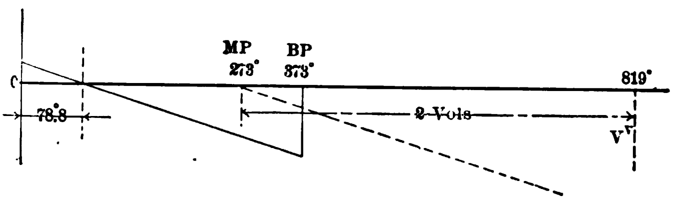
The formula for atomic stress $X + 26.24\,Z - a = 0$.
a equals $M\,P^{\circ} - 194.2^{\circ}$.

Average stress for class A $\dfrac{Z^{bp}}{2}$, for class B $\dfrac{Z^{bp} - Z^{s}}{2}$

$$\text{Energy (L.H.of V.)} = \frac{\text{Stress}}{2} \times \frac{M\,P + 273 \times \text{Val} - B\,P}{273}$$

WATER.

Final station $273 + 273 \times \text{Val}$	$= 819.$
Initial "	$373.$
Interval.	$446.$



$$\text{Strain of vol. } \frac{446}{273} = 1.633$$

Stress formula $X + 26.24\,Z - 78.8 = 0$. $X = B\,P = 373$.

$Z^{bp} = \dfrac{294.2}{26.24} = 11.218$. Energy $= \dfrac{11.218}{2} \times 1.633 = 9.158\ \mathcal{E}$

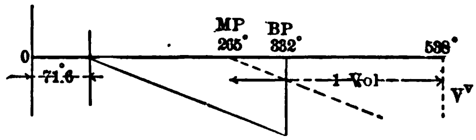
Energy of L. H. of V in unit mass $= 535.9 \times 17.96$ cals. $= 9624$ cals.

$$\text{Coef. B} = \frac{9624}{9.158} = 1051.$$

$$\text{Formula value } \frac{9.158 \times 1000}{17.96} = 510.5 \text{ cals. per gram.}$$

BROMINE.

Final station 265×1×273	= 538°
Initial station	332.
Interval	206.



$$\text{Strain of volume } \frac{206}{273} = 0.754$$

Stress formula $X + 26.24\,Z - 71.8 = 0.\quad X = B\,P = 332.$

$Z^{bp} = \dfrac{260.4}{26.24} = 9.9237.\quad$ Energy $= \dfrac{9.9237}{2} \times 0.754 = 3.744\,\text{€}$

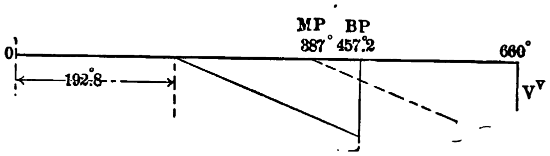
Energy (L.H. of V.) in unit mass $45.6 \times 79.76 = 3637$ cals.

$$\text{Coef. B} = \frac{3637}{3.744} = 971.3$$

$$\text{Formula value } \frac{3.744 \times 1000}{79.76} = 46.942.$$

IODINE.

Final station 387×1×273	= 660.°
Initial station	457.2
Interval	202.8



$$\text{Strain of volume } \frac{202.8}{273} = 0.7428$$

Stress formula $X + 26.24\,Z - 192.8 = 0.\quad X = B\,P = 457.2°$

$Z^{bp} = \dfrac{264.4}{26.24} = 10.\quad$ Energy $\dfrac{10}{2} \times 0.7428 = 3.714\,\text{€}$

Energy (L.H. of V.) in unit mass $23.95 \times 126.54 = 3030$ cals.

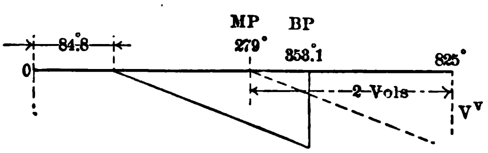
$$\text{Coef. B} = \frac{3030}{3.714} = 815.9$$

$$\text{Formula value } \frac{3.714 \times 1000}{126.54} = 29.35 \text{ instead of } 23.95$$

TABLE XII.

BENZENE C_6H_6.

Final st. $279 + 2 \times 273$	825°
Initial st.	353.1
Interval	471.9



$$\text{Strain of vol, } \frac{471.9}{273} = 1.7285$$

Stress formula $X + 26.24\,Z - 84.8 = 0$ $\quad X ¢ B P = 353.1$

$$Z^{bp} = \frac{268.3}{26.24} = 10.2326. \quad \text{Energy} = \frac{10.2326}{2} \times 1.7285 = 8.844\ \mathcal{E}$$

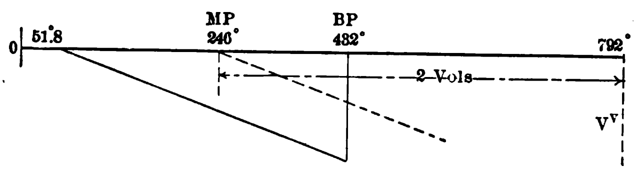
Energy of L. H. of V. in unit mass 109×78 cals. $= 8502$ cals.

$$\text{Coef. } B = \frac{8502}{8.844} = 961.3$$

$$\text{Formula value } \frac{8.844 \times 1000}{78} = 113.38 \text{ instead of } 109.$$

OIL OF TURPENTINE $C_{10}H_{16}$.

Final st. $246 + 2 \times 273$	792°
Initial st.	432
Interval	360



$$\text{Strain of vol. } \frac{360}{273} = 1.318$$

Stress formula $X+26.24\ Z-51.8 = 0.$ $X \not\in B\ P = 432°.$

$$Z^{bp} = \frac{380.2}{26.24} = 14.456. \quad \text{Energy} = \frac{14.456}{2} \times 1.318 = 9.554\ €$$

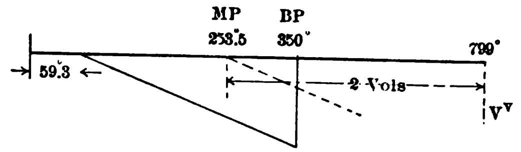
Energy of L. H. of V. in unit mass = 74 cals × 135.7 = 10042 cals.

$$\text{Coef. } B = \frac{10042}{9.554} = 1051.$$

$$\text{Formula value} = \frac{9554 \times 1000}{135.7} = 70.42 \text{ cals.}$$

CARBON TETRA-CHLORIDE $C\,Cl_4$.

Final st. 253×2×273	= 799°
Initial st.	350
Interval	449



$$\text{Strain of vol. } \frac{449}{273} = 1.6447$$

Stress formula $X+26.24\ Z-59.3 = 0.$ $X = B\ P = 350°.$

$$Z^{bp} = \frac{290.7}{26.24} = 11.078. \quad \text{Energy} = \frac{11.078}{2} \times 1.6447 = 9.11\ €$$

Energy L. H. of V. in unit mass = 57 cals. × 153.48 = 8748.3 cals.

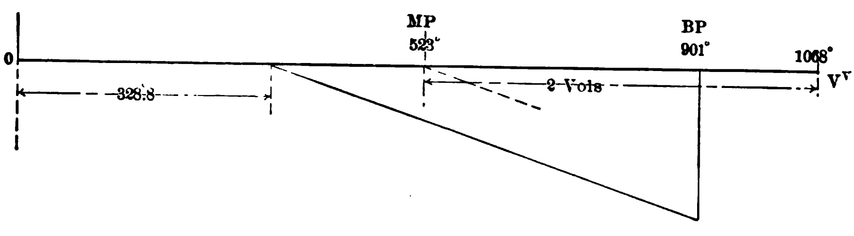
$$\text{Coef. } B = \frac{8748.3}{9.11} = 960.27$$

$$\text{Formula value of L. H. of V. } \frac{9.11 \times 1000}{153.48} = 59.312 \text{ instead of 57 c}$$

TABLE XIII.

STANNOUS CHLORIDE $Sn\,Cl_2$.

Final st. 523+2×273	= 1069°
Initial st.	= 901
Interval	168



$$\text{Strain of vol. } \frac{168}{273} = 0.61538$$

Stress formula $X + 26.24\,Z - 328.8 = 0.$ X @ $B\,P = 901°.$

$$Z^{bp} = \frac{572.2}{26.24} = 21.31. \text{ Energy } = \frac{21.31}{2} \times 0.61538 = 6.7096\,\text{€}.$$

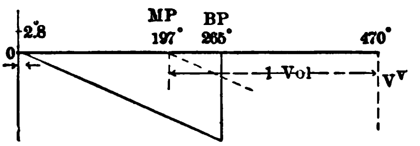
Energy L. H. of V. in unit mass $= 30.53$ cals. $\times\, 189.54 = 5773.3$ cals.

$$\text{Coef. } B = \frac{5773.3}{6.7096} = 862.4$$

Formula value L. H. of V. $\dfrac{6.7096 \times 1000}{189.54} = 35.399$ cals. instead of 30.53 as experimental val.

SULPHUR DIOXIDE.

Final st. $197 + 1 \times 273$	$= 470°$
Initial st.	265
Interval	205



$$\text{Strain of vol. } \frac{205}{273} = 0.7509$$

Stress formula $X + 26.24\,Z - 2.8 = 0.$ X @ $B\,P = 265°$

$$Z^{bp} = \frac{265}{26.24} = 10. \text{ Energy } = \frac{10}{2} \times 0.75 = 3.754\,\text{€}$$

Energy of L. H. of V. in unit mass $67 \times 64 = 4281$ cals.

$$\text{Coef. } B = \frac{4281}{3.754} = 1140$$

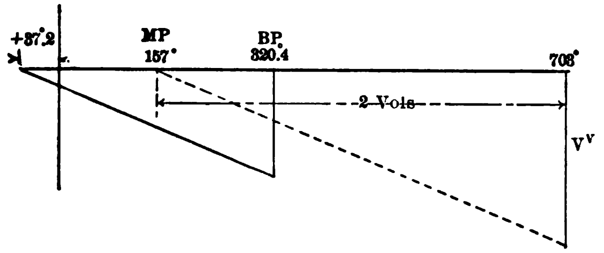
$$\text{Formula value} = \frac{3.754 \times 1000}{64} = 58.75 \text{ cals. instead of } 67.$$

* * * *

The following two cases fall in class B where the zero of stress falls beyond the absolute zero. On this account the average stress must be calculated as $\dfrac{Z^{bp} - Z^{z}}{2}$ where Z^{z} represents the calculated stress for $X = 0$.

CARBON DISULPHIDE CS_2.

Final st. $157+2\times273$	$= 703°$
Initial st.	320.4
Interval	382.6



$$\text{Strain of vol.} = \frac{382.6}{273} = 1.399$$

Stress formula $X+26.24\,Z+37.2 = 0.$ X @ $B\,P = 320.4$

$$Z^{bp} = \frac{320.4}{26.24} = 13.6279. \quad Z^z = \frac{37.2}{26.24} = 1.4176$$

$$Z^{bp} - Z^z = 13.6279 - 1.4176 = 12.2103$$

$$\text{Energy L. H. of V.} = \frac{12.2103}{2}\times 1.399 = 8.5426 \text{ Calors}$$

Energy L. H. of V. in unit mass 105 cals. $\times 75.89 = 7968.3$

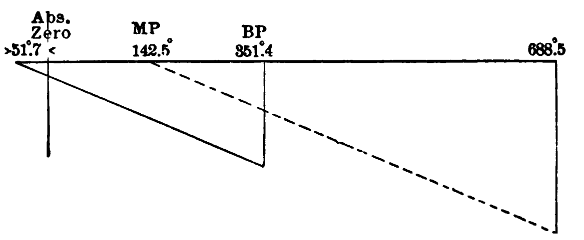
$$\text{Coef. } B = \frac{7968.3}{8.5426} = 932.8$$

$$\text{Formula value } \frac{8.5426\times1000}{75.89} = 112.5 \text{ cals. instead of } 105.$$

TABLE XIV.

ALCOHOL C_2H_6O.

Final station $142.5+2\times273$	688.5°
Initial station	351.4
Interval	337.1



$$\text{Strain of volume } \frac{337.1}{273} = 1.2348$$

Stress formula $X + 26.24\,Z + 51.7 = 0.$ X @ $B\,P = 351.4°$

$$Z^{bp} = \frac{403.1}{26.24} = 15.362. \quad Z^{s} = \frac{51.7}{26.24} = 1.970$$

$$Z^{bp} - Z^{s} = 15.362 - 1.970 = 13.392$$

$$\text{Cal. Energy L.H. of V.} = \frac{13.392}{2} \times 1.2348 = 8.2682 \text{ Calors.}$$

$$\text{L.H. of V. in unit mass} = 202.4 \text{ cals.} \times 45.88 = 9286.1$$

$$\text{Coef. B} = \frac{9286.1}{8.2682} = 1123.$$

$$\text{Formula value } \frac{8.2682 \times 1000}{45.88} = 180.21 \text{ cals. instead of } 202.4$$

SUMMARY OF RESULTS.

Name.	Experimental Tests.	Calculated Results.	Coefficient B.	Parts n.
Water	535.9	510.5	1051	2
Bromine	45.6	46.9	971.3	1
Iodine	23.95	29.35	815.0	1
Benzine	109.	113.1	963.7	2
Oil Turpentine	74.	70.4	1051	2
$C\,Cl_4$	57.	59.357	960.2	2
$Sn\,Cl_2$	30.53	35.39	862	2
$S\,O_2$	67.	58.75	1140	1
$C\,S_2$	105.	112.5	932.8	2
Alcohol	202.4	180.21	1123	2

Taking these results collectively they certainly offer favorable testimony regarding the truth of the various hypotheses we have made. They will be supplemented by others of a similar character.

The object of this exhibit is to cover an approximation of the latent heats of vaporization for as many substances as possible. It is understood, however, that in many of the cases recorded, the experimental determination is itself only an approximation, hence the variations shown from the theoretical.

There exists, however, a line of similar results for water, under evaporation at different temperature at constant pressure, where the results are exceedingly accurate.

They are by Regnault, but have been carefully revised by others owing to their importance in manufacturing processes.

It is proposed now to adapt our formula for this situation, which covers changes extending from zero to one hundred degrees centigrade.. Some of these results are shown on the following sheet. Our formula was designed to cover the evaporation of water from the boiling-point @ 100 C. under atmospheric pressure. This station naturally forms one of the limits of the new series of experiments. In this formula the term $B\ P$ occurs twice, as can be seen below:

$$\text{Energy (milligram molec).} = \frac{M\ P^{o} + 273\ n^{o} - B\ P^{o}}{273} \times \frac{-Z^{bp}}{2} \epsilon$$

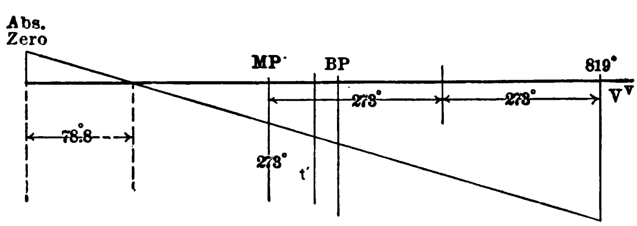
1st. It determines the value of the internal stress $-Z$ in the equation $X + 26.24\ Z - (M\ P^{o} - 194.2^{o}) = 0$.

2d. It is found in the first term, where it determines the volume through which the given stress is developed.

The term $\frac{-Z^{bp}}{2}$ however expresses the final stress which must exist within the vapor to enable it to overcome the atmospheric pressure and to disperse. Under the conditions reigning in the new series of experiments this pressure is to be constant.

Hence the value $\frac{-Z^{bp}}{2}$ must also be constant as representing the condition to which the material must always be brought in order that evaporation may ensue. It culminates also at the above mentioned limit.

But the second value of $B\ P$, the one determining the state of expansion, as found in the term $\frac{M\ P + 273\ n - B\ P}{273}$, requires change. In measuring the latent heat, as the energy still to



be acquired by expansion from some initial station t° to a final one V^{v}, where gasification is complete, we assumed that two volumes of expansion were requisite for water, as a compound, to measure the energy of the unit mass.

Thus our final station fell at $V^{v} = 273 + 273\,n = 819^{\circ}$ while originally our initial station fell at the boiling-point.

But it is desired now to include the conditions where the evaporation falls at lower temperatures, and we can then describe this initial station as the temperature of evaporation t°.

$$\text{Energy (milligram molec)} = \frac{M\,P^{\circ} + 273\,n - t^{\circ}}{273} \times \frac{-Z^{\text{bp}}}{2}$$

Under this simple change of formula we estimate the energy expended under constant atmospheric pressure within a volume that is varied by alterations in its initial station, the temperature t° of evaporation. We are thus able to vary the strain of volume to cover the several conditions reigning within the desired series of experimental states.

Determinations under this change have been calculated for a number of values of t° and the results are shown in Table XV and on Chart F.

Columns 2 and 3 give the various initial stations t° chosen, both in centigrade and absolute centigrade degrees.

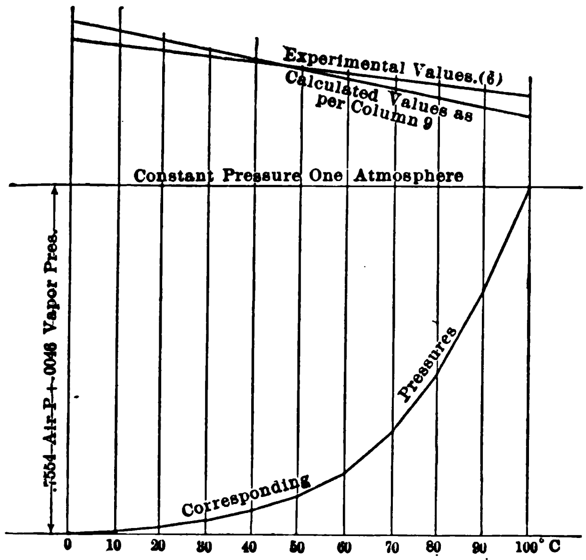


CHART F.

The experimental results cover differences of one degree, but we have chosen differences of ten degrees, as covering fully all that need be shown to prove our case.

Column 1 gives the vapor pressure found in the atmosphere at these stations. These values have also been charted and in such a manner that 760 mm. $- V P$ represents the balance of pressure due to the air alone at each station.

Column 4 gives in calories the experimental values of the latent heats of vaporization of one gram of water.

In column 5 these values are divided by 1000, showing the corresponding values in Calors for milligram units.

Column 6 gives the product of the latter into 17.96 as the unit mass of water. Hence these experimental values are recorded as the latent heats of vaporization in Calors for comparison with the direct results calculated from our formula.

Column 7 shows the constant value of the stress $\frac{-Z^{bp}}{2}$ equalling the atmospheric resistance.

Column 8 shows the varying strain of volume $\frac{819 - t^{\circ}}{273}$.

Column 9 gives the product of stress and strain of volume.

Its values are directly comparable with the experimental ones in column 6.

Column 10 shows the percentage of these values.

The results when charted show that under medium temperatures the values are identical, that at low temperatures the calculated results are somewhat higher, and under high temperatures the reverse conditions ensue. Still, the close correspondence in values seems to indicate that the energy of change must be measured, as claimed, as that of the unit mass, and that it can be covered by the product of the internal stress $\frac{-Z}{2}$, when developed through the actual volume of change under these methods.

The Origin of Perfect Gas.

With vapors and superheated gases representing the negative and positive conditions.

From the foregoing study of the situation at the boiling-point under atmospheric pressure, we have apparently to distinguish

TABLE XV.

Regnault's experimental results compared with calculated data of L. H. of V. for water.

$$\text{Energy (mgrms molec)} = \frac{M\ P^\circ + 273\ n^\circ - \text{evap. temp}^\circ}{273^\circ} \times \frac{-Z^{bp}}{2} \text{€}$$

Energy (unit mass) = molec wgt × L. H. of V. under constant barometer (at 760 mm).

Molec wgt = 17.96 mgrms. t° = temp. of evaporation. $B\ P$ = 373° a. c.

1 Vapor Pressure in mm. Hg	2 Temp. Cent.	3 t° temp. of Evaporation. a. c.	4 Latent Heat in calories. 1 gram vapor.	5 Latent Heat V in €alors 1 milligram.	6 Latent Heat of V. €alors per unit mass. 17.96 mgms.	7 $\frac{-Z^{bp}}{2}$ under const. pres. 760 mm. log. = 0.74888	8 Variable volume $\frac{819^\circ - t^\circ}{273}$	9 Calculated L. H. of V. in €alors per unit mass; compare with column 6	10 % of values in columns 6 and 7 $\frac{\text{col. 6}}{\text{col. 9}}$
4.6	0°	273°	606.5	0.6065	10.8927	5.609	2.	11.218	96.29
9.2	10°	283°	599.54	0.59954	10.768	5.609	1.963	11.012	97.77
17.4	20°	293°	592.59	0.59259	10.643	5.609	1.926	10.808	98.48
31.5	30°	303°	585.62	0.58562	10.517	5.609	1.890	10.601	99.21
54.9	40°	313°	578.64	0.57864	10.392	5.609	1.853	10.396	99.96
92.	50°	323°	571.66	0.57166	10.267	5.609	1.817	10.191	100.7
148.	60°	333°	564.66	0.56466	10.141	5.609	1.780	9.985	101.5
231.	70°	343°	557.64	0.55764	10.015	5.609	1.743	9.78	102.4
354.	80°	353°	550.61	0.55061	9.888	5.609	1.707	9.574	103.28
525.5	90°	363°	543.56	0.54356	9.762	5.609	1.670	9.369	104.2
760.	100°	373°	536.5	0.5365	9.6355	5.609	1.633	9.060	105.1

Experimental data. Calculated data.

two stations at this temperature with a period of change lying between them.

These stations are: 1st, the liquid condition at *B P*; 2d, the gaseous condition at *B P*.

Under the former we find the liquid supplied simply with its sensible heat, and at the temperature where its internal atomic stress just balances the atmospheric pressure.

In the second we find gas just rising from the liquid. In the interim, however, a change of aggregation must be prepared for. The energy of the unit mass, as the cohesion of the liquid, must be developed by heat to its maximum limit in order to free the molecules and to permit them to rise in gas form.

Naturally this change cannot occur when the particles are still tied together. To free them, the energy of the mass must be developed to the state where it is equalled by that of expansion, as in the Calory where $\frac{\text{Energy Mass}}{\text{Energy Vol.}} = 1$, or where the matter becomes homogeneous.

As matter at the boiling-point is held to atmospheric conditions this expansion must equal n volumes of 273 degrees of change from *M P* as origin of the gaseous expansion.

Then n expresses the proper value relative to the valency, or the density, of the material in question, *i.e.*, the number of parts expanding simultaneously when we are balancing the compressive energy of the atmosphere.

Thus we reach the gaseous condition at *B P* where the added portion of heat energy equals that of the latent heat of vaporization and where the volume described locates our station V^{v} on the chart.

But, owing to existing conditions, we find that this second state at *B P* is one not easily maintained. Hence matter can exist in two forms at this station.

These are: 1st. The one just described, where the rising particle holds the full latent heat of vaporization. But as this quota of heat energy is held by expansion without change of temperature, trifling losses, which increase rapidly by contact with other bodies, are made almost instantly.

2d. The vaporous form appears.

For instance, the familiar case where steam is escaping from

a boiler at low pressure into the atmosphere. At first the gas is invisible, but within a short distance of the orifice from which the product flows, it assumes the form of vapor, being opaque, of white color, and hence readily seen owing to a slight loss of heat energy by contact with the air. When exposed then to contact with other particles some loss of the increment is made instantly and the vapor form originates.

This loss can increase until it involves the entire amount of the latent heat, when the matter returns to the liquid form.

Vapor can then have various charges of heat energy. But, when under atmospheric conditions this vapor is reheated and its temperature gradually approaches that station we have designated as V^v it can slowly regain this lost energy as sensible heat in the gaseous state.

Then at V^v, under this condition, it will once more be in possession of its full quota of heat energy, and it will again have driven off the last remnant of cohesion of the vaporous state.

This energy of sensible heat acquired in the gaseous condition, it cannot lose without a change of temperature. Hence the product must now have reached the condition of a perfect gas, and under still higher temperatures will act as such.

Then, as stated by Regnault, its specific heat will not vary with the temperature, for as described it must be possessed of its latent heat of vaporization.*

This condition is reached with bodies possessing low boiling-points when held at laboratory temperature, because their particles hold heat energy in excess of their energy of cohesion and they cannot lose the same by contact with neighboring particles.

At *B P* then, under suitable pressure, and at V^v, under atmospheric conditions we have material in such a state that all cohesion of the liquid and solid states are balanced by heat energy.

At the station thus defined, we can place the zero condition, the origin of the perfect gas.

When heated above this station all increase of energy must be heat energy. Hence we can distinguish this state as the

*But before reaching this station its specific heat will vary as with each degree of change some quota of the latent heat must be recovered.

" superheated " indicating the possession of an excess over and above that inherent in the material under atmospheric condition.

Then this condition may be known as positive to the zero condition. On the other hand we can recognize as the vaporous and negative condition any one wherein the heat energy held is below the zero stage.

Possibly we can trace the changes towards this form best when we follow those met with by water, for the losses undergone by this body are greater than any other, as its latent heat of vaporization is also greatest. As stated, the vaporous form follows loss of energy from *B P*. But *B P* is a variable station owing to possible changes in the atmospheric pressure.

Hence in high altitudes when *B P* approaches *M P* with increasing values of latent heat, we have very marked conditions of this vaporous and negative state. For, we must recognize that while such vapor can undergo change, or the loss of heat energy, at high altitudes, it can only reacquire a portion of this heat when transported to lower stations under greater pressure.

Hence even at low temperatures vapor can exist under atmospheric conditions and is in a position to promote transference of energy to and from other matter.

In proportion to this loss of heat energy that of cohesion of the liquid must return, and we have a means presented whereby matter is drawn to contact with other bodies.

Personally we recognize the presence of water vapor, when diffused in the atmosphere even in infinitesimal amounts, by a damp and chilly feeling. In this condition it is often able to originate chemical reaction in foreign bodies by creating a negative condition, or one where some of the constituents are short of heat energy in the presence of others that are superheated, for contact is brought about and the condition resulting often becomes favorable for neutralization.

Thus while itself only subject to physical change, in the vaporous state, it is able to stimulate change in others.

This situation is proved by the fact that these reactions can often be restrained by the removal of moisture, or of water in vapor form.

But to return to the main question, it can be noted that,

from other positions of V^v relative to the boiling-point, another marked condition can be traced.

On Chart E this situation is shown in the monads *Na* and *K*, as well as in the triads *Bi* and *Sb*.

Here the station V^v falls before the boiling-point for with monads n equals one and with triads n equals three, and these stations, thus described, fall inside of the boiling point under atmospheric pressure.

From this point of view the condition required to measure the energy of the mass by that of volume, or where $\frac{\text{Energy Mass}}{\text{Energy Vol.}} = 1$, and where the results can be commensurate with the Calory, arrives before that of the boiling-point under atmospheric pressure.

Hence these bodies, in that condition, may also be called superheated, for they must be raised to a higher stress before they can gasify under atmospheric pressure. With this surplus they must also have a tendency developed towards chemical combination.

When thrown in contact with oxygen superheated at laboratory temperature, similar bodies when roused by a stimulating influence of sufficient force, such as contact with flame, an electric spark, water vapor, or even sunlight tend to unite chemically under fixed conditions. Others unite directly under these circumstances. But these fixed conditions are those we have called standard or normal where the unit masses are held in n unit volumes.

Then the surplus energy these masses hold must be freed, for the product even when of low boiling-point and superheated, cannot hold the surplus energy of all the constituents.

This class of combination has been called combustion, but if the gases are confined it becomes an explosion.

Combinations of this character are then originated by extraneous causes, while those resulting from ionization are from internal.

Naturally if the reaction is once started from either cause the whole energy of the atom becomes involved instantly.

But if the vaporous condition can be indicated as a negative one relatively to the internal condition of a perfect gas at its point of origin *B P* under specific pressure, then the super-

heated gases can be designated as positive relative to the same situation, for they hold a greater amount of heat energy than is required by the material constitution, or the configuration, while the vaporous ones hold less.

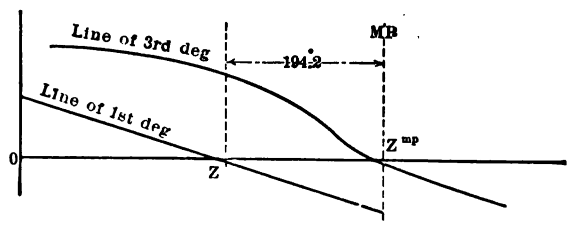
Then the zero condition of the perfect gas must be recognized as that one where under some fixed atmospheric resistance the material has reached at V^v that condition of sensible heat which replaces the entire charge of the latent heat due under n volumes of change from $M\ P$ as the origin of the gaseous expansion.

At this station the development of internal energy has been brought to the standard and is commensurate with that of the Calory, for in this latter experimental determination the total internal and physical change of one kilo of mass is measured as that of one volume of homogeneous matter during a change of one degree.

The Situation at the Melting-Point.

If, in the study of chemical change, we turn our attention to the conditions found at the melting-point, we can recall several items of interest, relating thereto, that have already been mentioned.

1st. In the study of the cubic formula, we found the zero of stress (gaseous) to be located at this point, with an increase



of 1/273 per degree of change. Thus we had an indication that the gaseous volume originated also at this station.

2d. The known constancy of this gaseous expansion in all matter combined with the above mentioned result, gave us a constant form of equation of the first degree, applicable to all matter and representing the internal atomic pressure in the various changes during rising temperature.

3d. Under these conditions another state of constancy revealed itself, under this equation, at $M\ P^{\circ} - 194.2^{\circ}$ locating a zero of internal stress.

4th. Under the supposition that the energy developed during physical change was represented by the development of energy through the changed volume under atmospheric pressure and constant temperature, we were able to calculate approximations to the experimental values of the latent heats of vaporization.

5th. For this purpose the idea was broached that the cohesion of the chemical mass as a unit was represented by the volume of expansion developed in a system under changes of periods of 273°, in relations required by the number of parts expanded simultaneously.

Now it is proposed to show that for stations between absolute zero and *M P* a different condition exists.

Here the parts are evidently still in contact, owing to the intensity of the cohesion of the solid, and it is only at the final station *M P*, where a freedom of motion is possible, that liquidity results, and though in the exchange between the energy of mass and that of motion by heat a rate of change exists, it must vary from that previously mentioned.

As the zero of atomic stress lies at $M\ P^{\circ} - 194.2^{\circ}$ this station can be regarded as the initial one and the constant period presented by all matter between this initial and our chosen final station *M P* must determine the constant rate of energy change, the atomic heat, which is recognized in its connection with the solid state, for here the last traces of that condition are disappearing.

In the cubic equation the angle of the straight line, with the abscissa, when leaving *M P* determines a constant relation between our ordinates, equal to 1/273.

Similarly the relation of the new ordinates of the equation of the first degree ought to indicate some constant relation and should claim our attention.

This point becomes of interest when we recognize that $(193.03)^2 = 1/2\,(273)^2$ and that without doubt 194.2° is an approximation to a more accurate value 193.03.

By our methods, these periods of change can be recognized as those necessary to develop the energy of cohesion of certain masses through heat. If therefore we represent by 273 that of the full unit mass, then 193.03 must represent that of the half mass.

They are both expressed as squares, for cohesion increases

proportionately to the square of the mass. Their relations are then indicated by the amounts of expansion required to develop the comparative energies of cohesion.

From this point of view, we should judge that the constant mass referred to, as controlling the situation below *M P* was the half mass, the unit of cohesion. Then the heat energy developed to this station must bring the material to that standard condition where the energy of cohesion of the half mass towards its neighbor, is balanced.

This statement recalls the decision of Regnault that the thermo-atomic weights were the halves of the chemical units, when measured relatively to hydrogen.

The value 193.03 would then be as nearly correct as the period of expansion 273° expresses that of the full volume.

In the following calculations, however, the original value of 194.2 is retained, since even the value 273 is known to be only an approximation. Our value is also sufficiently accurate to indicate the principles involved, and it is believed that later a more accurate result can be arrived at, with which a comparison of our methods can be made.

In order to estimate the constant rate of energy development by the physical change occurring below *M P* and accruing during the period of 194.2°, we have:

$$\text{Constant energy} = 1/2\, Z^{mp} \times \frac{194.2}{273} \text{ Ɛalors.}$$

Thus again we have the energy held represented, in Ɛalors, by a product of the average stress into the volume of expansion, but now with a lesser mass, and a prescribed period of change, determining a new local rate.

As we shall shortly be obliged to distinguish this condition at *M P* from another holding a somewhat larger amount of energy, it is desired to designate this original constant as the minimum.

$$\text{Then: Stress} - Z^{mp} = \frac{194.2}{26.24} \quad \begin{array}{l} \text{log. } 2.2882492 \\ \text{''} \quad \underline{1.4189678} \\ \quad\;\; 0.8692814 \text{ antilg. } 7.4009 \end{array}$$

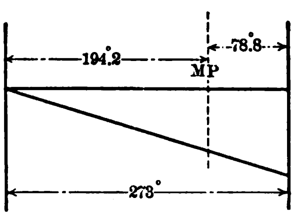
$$\text{Vol} = \frac{194.2}{273} \quad \begin{array}{l} \text{log. } 2.2882492 \\ \text{''} \quad \underline{2.4361626} \\ \quad\;\; \bar{1}.8520866 \text{ antilog. } 0.71135 \text{ Vol.} \end{array}$$

Then the minimum energy held at $M\ P$ by a mass represented by the 1/2 atomic weight is:

$$\text{Min. E.} = \frac{7.4009}{2} \times 0.71135 \text{ Calors} = 2.6323 \text{ C}.$$

Thus, then, we have an expression for the minimum and at the same time a constant amount of energy, required to overcome the cohesion of the half mass when calculated from the atomic pressure exerted through this prescribed period of 194.2°.

If we double the value of this constant, we can recognize its similarity to the well known constant 5.2 called the atomic heat. But it is well known that at $M\ P$ a change of aggregation occurs. Without a change of temperature a certain free-



dom of motion between the parts, or liquidity originates, probably from a loss of contact between the molecules.

Under this freer motion, still caused by heat, a different condition of equilibrium can result, at the same temperature.

Under the same atomic pressure, therefore, and still at the melting-point, but in a somewhat larger volume owing to the new condition, a new balance of the energies of cohesion and heat can be found.

Here, however, we are at the melting-point the origin of the gaseous stress and of the gaseous volume. Here, the cohesion of the half mass, carrying the minimum atomic heat, because it is limited and measured by an expansion of 194.2° with its parts in contact, can now expand under the gaseous stress and volume, until it is measured by a new limit, that of an expansion of 273°. This state, representing another equal distribution of the energy of mass to that of volume, is the standard one.

It holds, however, a greater amount of energy in this new condition, and it will be shown later, that this added incre-

ment, thus accurately defined, represents that of the latent heat of fusion.

The energy of heat that can be developed under change from the origin of the atomic stress to the origin of the molecular condition, or to the melting-point, represents that of cohesion under a fixed limit, *i.e.*, that of the half mass or half atom.

We have determined it as a constant for all known bodies that present themselves as aggregations of matter. In fact, it seems to prescribe the very conditions of their existence.

Possibly it expresses the fact that under an established configuration, determining the rate of mass to volume acting, a certain resultant of attraction must materialize between the aggregations of common ultimate particles. Under change this resultant decreases as $-Z$ increases while the volume grows.

During the measured change alluded to above we found that the interval 194.2° as well as the average stress $\frac{Z^{\mathrm{mp}}}{2}$ were constant. Therefore, the continual accumulations of heat energy occurring can vary only in two ways.

First. With the rate at which the energy of mass is balanced by that of volume at the chosen station; in other words, with the rate under which mass is bound by cohesion in each case, as for instance whether it is equal to one, two or more volumes of expansion.

Second. With the rate at which heat energy can be accumulated by the body during change.

These provisos really cover the same situation when considered from the different points of view of heat and cohesion.

The rate at which mass is bound by cohesion to the condition of a unit mass is expressed by the atomic weight, and it is evident from the irregular gaps occurring between those of known elements that the prescribed condition can reoccur only after variable periods of increase.

As measured by heat energy our methods prescribe a minimum condition covered by an expenditure of 2.6323 ϵ per unit of cohesion, this amount being necessary to measure the energy of cohesion between our stated limits.

At our final station *M P* a freedom of motion originates and our unit being at the origin of the gaseous volume becomes subject to a different rate of expansion.

At the same time this half mass, the unit we are discussing, has only been submitted to a fractional expansion of $\frac{194.2°}{273.}$ It must therefore contain some residual cohesion.

Under the generalization expressed by the curve of the atomic volumes, the energy of the unit mass must be determined by some complete unit volume of condition, which can be expressed by

$$\frac{\text{Mass}}{n.\ \text{Vol.}}.$$

In the gaseous condition which it has now reached we can compare it with others under Regnault's law of the equal thermal capacity of equal unit volumes, when the expansion of 273 degrees covers that of the unit volume.

The volume under the new rate of expansion can be estimated as $\frac{273° - 194.2°}{273°} = \frac{78.8°}{273°} = 0.28865.$

Then under the conditions as described the maximum energy of this change, for our smaller unit can be written:

$$2.6323\,\text{€} \times 1.28865 = 3.39174\,\text{€}.$$

The latter portion of this charge is isothermal. Therefore, this added portion of energy can readily be lost to surrounding bodies. Cohesion must then return to a corresponding extent.

Thus again we find a station where a negative condition can originate under a loss of this character. It is to be found where the fluid condition originates under atmospheric pressure. Under solution many reagents meet this condition, others are superheated at room temperature owing to the values of their melting-points.

Returning to the main question, it is evident that the half mass must hold a maximum energy, or Max. E. = 3.39174 € at our final station $M\,P° + 78.8°$. It is also clear that the total amount of energy held in the molecular condition must still be dependent upon the number of parts n present and subject to expansion.

On the other hand, it is clear that unless sufficient energy of cohesion is present to bind these fixed quotas of heat energy in each case, the prescribed aggregation cannot persist, even if formed. In other words the existence of this stated amount of cohesion is an absolute necessity for the formation or the

continuance of a body, as an aggregation of matter under a fixed rate of mass to volume.

It is the existence of this cohesion which determines first the half mass and thus indirectly the whole. Naturally, without this amount of cohesion there is no bond of union and matter will gradually disperse.

If the above mentioned hypothesis were true, matter could have a common origin; its various persistent aggregations must simply reach a fixed initial condition of mass to volume under a constant expenditure of energy for each.

This condition seems to express the generalization of the curve of the atomic volumes.

Our constant Max. E. as 3.39174 € recalls the value 6.7 known as the atomic heat.

We can now revert to the second condition we have cited in stating this problem, for, as stated, it refers to the same development of physical change we have been discussing.

It naturally refers to the rate under which this maximum heat energy can be accumulated by bodies and therefore to their specific heat.

Under any rate of accumulation of this energy, the density of the material will have great influence in determining the station held by the melting-point.

It is common knowledge that high melting-points fall with great density while low ones accompany lesser densities.

Density, however, is expressed as a rate of mass to volume and this generalization declares that the greater the mass to volume, the greater the number of parts *n* present to absorb the heat energy, the higher the melting-point will fall.

Under the conditions we are discussing this unit of mass to volume requires $\frac{2.6323\,€ \times 1.28865}{1/2\ \text{At. Wt.}}$ to balance the energy of cohesion.

As *n* such parts are found developed from absolute zero to the melting-point, the energy locally spent can be written

$$M\,P \times n\,\frac{2.6323\,€ \times 1.28865}{1/2\ \text{At. Wt.}} = \text{Energy}.$$

This same energy can, however, be expressed under change by units of degree and weight as $M\,P \times$ Spec. Heat = Energy, or Spec. Heat $= n \times \frac{2.6323\,€ \times 1.28865}{1/2\ \text{At. Wt.}}$

Thus we arrive at the Garnier Cannizzaro generalization for the determination of the specific heat of compound bodies.

If, however, we assume n equal to unity, thus covering the conditions where simple half atoms are in presence of each other in the solid state, we have the formula expressing the value of the specific heats of elements in that condition.

If, then, we consider these constants 2.6323 € and 2.6323 € × 1.28865 or 3.39874 € as independent units of atomic heat expressing under different conditions the energy accumulated under the atomic pressure by each half atom at the melting-point, we have only to divide them by the half atomic weights to reach the unit capacity of energy of each per degree and per unit of weight as well as with $n = 1$.

The values determined from the maximum capacity will yield theoretical specific heats, as $\frac{2.6323\ € \times 1.28865}{1/2\ \text{At. Wt.}}$

The minimum condition can be represented by $\frac{2.6323\ €}{1/2\ \text{At. Wt.}}$

On Tables XVI and XVII two series of results are shown representing these quotients. Adjoining these two columns is shown one marked " accepted values of Spec. H (solid) " for comparison with those of Max. E; while also a few cases are noted, in a second column where some experimental values approach those of Min. E.

Our methods seem then to fall into line with experimental results, and to indicate that when accurate determinations of our coefficients are made, it will be possible to determine theoretical values for these specific heats.

We must bear in mind, however, that many of the experimental values have been determined at temperatures far below the melting-points of the materials under observation.

If we wish to examine the conditions resulting when two or more elementary atoms unite to form a compound, we must turn to the conditions covered by the Garnier Cannizzaro generalization, which may be expressed as follows:

$$\frac{A \times C}{n} = \text{Constant.}$$

Here A equals the formula weight of a compound and C the specific heat, while n represents the number of parts that are found in the molecule of the compound subject to expansion.

TABLE XVI.

Energy of Cohesion per Units of Change and Degree, or the Specific Heat.

$$\text{Min. E} = \frac{2.6323\ \epsilon}{1/2\ \text{A. Wt.}}.\ \text{Spec. H } (s) = \frac{2.6323\ \epsilon \times 1.28865}{1/2\ \text{A. Wt.}} = \frac{3.39174}{1/2\ \text{A. Wt.}}\ \epsilon$$

Name.	1/2 A. Wt.	Min. E	Max E	Accepted Spec. H (s)	
H.	0.5	5.264	6.783		
He.	2.	1.316	1.695		
Li.	3.555	0.7521	0.96907	0.941	
Be.	4.502	0.5847	0.7533		
B.	5.45	0.483	0.6223	0.5 ?	
C.	5.985	0.4399	0.5667	0.463	
N.	7.	0.376	0.4845		
O.	7.98	0.3298	0.425		
Fl.	9.503	0.277	0.3569		
Ne.	10.	0.26323	0.3391		
Na.	11.5	0.2289	0.2949	0.293	
Mg.	12.15	0.2161	0.2791	0.25	
Al.	13.52	0.1947	0.2508	0.225	
Si.	14.15	0.18603	0.2397	0.203	0.181 graph.
P.	15.48	0.170	0.219	0.202	0.174
S.	15.99	0.1646	0.2121	0.209	0.163 Rhmb.
Cl.	17.68	0.1488	0.1918		
K.	19.515	0.1348	0.1738	0.166	
Ca.	19.956	0.1319	0.1699	0.170	
Ar.	20.	0.1316	0.1695		
Sc.	21.985	0.1197	0.1542		
Ti.	24.	0.1096	0.1431	0.1485	
V.	25.55	0.1030	0.1327		
Cr.	26.225	0.1003	0.1293	0.10	
Mn.	27.4	0.0960	0.12378	0.122	
Fe.	27.94	0.0942	0.12139	0.114	
Ni.	29.35	0.08968	0.11551	0.108	
Co.	29.68	0.08869	0.1141	0.117	
Cu.	31.59	0.08332	0.1073	0.1013	0.08847
Zn.	32.55	0.0887	0.1042	0.1015	0.0955
Ga.	34.95	0.07531	0.0970	0.079	
Ge.	36.16	0.07279	0.9379	0.077	
As.	37.45	0.07028	0.0956	0.09058	0.0758 amph.
Se.	39.435	0.06675	0.086	0.0861	0.0675
Br.	39.88	0.066	0.08504	0.0843	
Kr.	41.	0.0642	0.08272		
Rb.	42.6	0.06179	0.07961		
Sr.	43.6	0.06043	0.07786		

TABLE XVII.

Energy of Cohesion per Units of Change and Degree, or the Specific Heat.

$$\text{Min. E} = \frac{2.6323\ \mathfrak{E}}{1/2\ \text{A. Wt.}}.\quad \text{Spec. H } (s) = \frac{2.6323\ \mathfrak{E} \times 1.28865}{1/2\ \text{A. Wt.}} = \frac{3.39174\ \mathfrak{E}}{1/2\ \text{at. wt.}}$$

Name.	1/2 A. Wt.	Min. E	Max E.	Accepted Spec. H (*s*)	
Y	44.45	0.05922	0.076305		
Zr.	45.2	0.053238	0.075038	0.0666	
Nb.	46.85	0.056186	0.072396		
Mo	47.95	0.054897	0.070735	0.07022	
Rh.	52.05	0.050573	0.065163		0.05803
Ru.	51.75	0.050866	0.065541	0.0611	
Pd.	53.1	0.049573	0.063874	0.0593	
Ag.	53.83	0.04890	0.06300	0.057	
Cd.	55.85	0.047132	0.06072	0.05938	
In	56.8	0.04634	0.05971	0.057	
Sn.	59.4	0.044315	0.05710	0.0562	
Sb.	59.8	0.04401	0.05671	0.0523	0.047
Te	62.5	0.04211	0.05426	0.05161	0.0475
I	63.27	0.041605	0.05360	0.0541	
X	64.	0.04113	0.05299		
Cs	66.35	0.03967	0.05111		
Ba	68.45	0.03845	0.04955		
La	69.	0.03814	0.049156	0.0449	
Ce	70.6	0.03728	0.04804	0.0448	
Ta	91.	0.028926	0.03727		
W.	91.8	0.02867	0.03694	0.03636	
Os.	95.5	0.02756	0.035515	0.0331	
Ir.	96.25	0.02734	0.035239	0.0363	
Pt.	97.15	0.02709	0.03491	0.0343	
Au.	98.35	0.026765	0.034486	0.0324	
Hg.	99.9	0.02635	0.03395	0.0319	0.0262
Tl.	101.85	0.02589	0.03330	0.0335	
Pb.	103.2	0.02550	0.03286	0.0315	
Bi.	103.65	0.02539	0.032716	0.0373	0.027
Th.	116.	0.02268	0.029239	0.0276	
U.	119.5	0.022028	0.028383	0.028	
Limit	128.86	0.020429	0.026323		

From experimental evidence it appears that the formula weight must assume the place of the half mass, as the unit of cohesion. In other words, twice as many parts must be present, as are described in the formula, under values of *n*.

This recalls the "Law of Even Numbers" formulated by Gerhardt and Laurent, which has been confirmed by many analyses.

Beyond this duplication of parts, however, the factor *n* has a specific value, in each case.

TABLE XVIII.

Energy of Cohesion in Compounds per Units of Change and Degree.

$$\text{Min. E} = \frac{n \times 2.6323\ \text{€}}{\text{Mol. Wt.}}.\ \text{Max E.} = \frac{n \times 2.6323\ \text{€} \times 1.28865}{\text{Mol. Wt.}} = \frac{3.39174\ \text{€} \times n}{\text{Mol. Wt.}}$$

Name.	Mol. Wt.	*n*	Max. E.	Accepted Sp. H (*s*)	Molec. Ht.
Li Cl	42.38	3	0.2401	0.2650	10.175
Na Cl	58.365	4	0.22715	0.23	13.567
K Cl	74.42	4	0.1823	0.184	13.567
Rb Cl	120.57	4	0.11252	0.112	13.567
NH_4Cl	53.37	6	0.381131	0.390	20.350
Ag Cl	142.97	4	0.09489	0.091	13.567
S Cl	67.37	4	0.2013	0.2024	13.567
$Ca\ Cl_2$	110.65	4	0.1226	0.1102	13.567
$Ca\ Cl_2$	110.65	6	0.1839	0.194	20.35
$Ca\ Cl_2\ 6H_2O$	218.65	26	0.403	0.406	88.185
$Ca\ Cl_2\ 6H_2O$	218.65	40	0.620	0.628	135.67
$Sr\ Cl_2$	158.04	6	0.1287	0.1199	20.350
$Ba\ Cl_2$	207.64	6	0.098	0.0902	20.350
$Ba\ Cl_2\ 2H_2O$	243.67	12	0.1670	0.171	40.70
$Pb\ Cl_3$	312.51	6	0.0651	0.0664	20.35
Cr_2Cl_5	317.12	12	0.1283	0.143	40.70
$Mn\ Cl_2$	125.54	6	0.1622	0.14255	20.35
Cu Cl	98.25	4	0.13808	0.13824	13.567
$Mg\ Cl_2$	95.04	6	0.2142	0.1946	20.35
Hg Cl	235.37	4	0.05762	0.0520	13.54
$Hg\ Cl_2$	270.74	6	0.07516	0.715	20.35
$P\ Cl_3$	137.11	8	0.1979	0.1987	27.134
$As\ Cl_3$	181.01	9	0.1686	0.176	30.525
Ice H_2O	18.	3	0.5652	0.56	10.175
Column 1	2	3	4	5	6

From the last equation we have:

$$C = \frac{n \times \text{Const.}}{A} \text{ or } \frac{n \times 2.6323\, \epsilon \times 1.28865}{\text{Molecular weight}} = \text{Specific Heat.}$$

On Table XVIII the results of this formula have been tabulated for twenty-four cases, mainly compounds of chlorine.

Many others could readily be obtained, but these seem ample for our purpose.

In column 4 are shown the calculated values of the specific heats, for comparison with those of column 5, the experimental ones. In columns 2 and 3 respectively are shown the values of the molecular weights, and those of n.

In column 6 the molecular heats are shown.

As they are determined here, the values of n have a considerable range, reaching, in the few examples given from 40 to 3.

There is also given an application of our method to a test of experimental determinations of the specific heat of solutions.

Here n is sought, representing the number of parts or of volumes expanding. Two cases are shown, and in each part n is calculated for two conditions, which are to be compared.

These conditions are purposely selected so that double the amount of water is present, thus giving an experimental determination of the relations of n.

Their observed specific heats, as well as their molecular weights, are used in the calculations.

The calculated values of n are then found expressing how many parts or volumes carry the equivalent of the constant.

Again a considerable range of values is indicated. But lastly, by taking the relation to each other, we find $\frac{n'}{n''} = \frac{\text{Vol}'}{\text{Vol}''} = 2$, confirming the experimental condition.

Specific Heat of Solutions.

Test of two pairs of experimental determinations.

$$n = \frac{\text{Mol. W} \times \text{Spec. H.}}{\text{Const.}}$$

Molec. Wt K C1 = 74.42 grams.
1 Aq. Molec. wgt = 18. grams.

K C1 + 15 Aq = 344.42 gr @ Sp. H 0.761 makes n' = 77.277

K C1 + 30 Aq = 614.2 gr @ Sp. H 0.850 makes n'' = 143.979

then n'/n'' = 1.99256.

$K\,Cl + 50\,Aq = 974.42$ gr @ Sp. H 0.904 makes $n' = 259.712$
$K\,Cl + 100\,Aq = 1874.42$ gr @ Sp. H 0.948 makes $n'' = 523.904$
then again $n'/n'' = 2.01725$.

It may be well to note that the formulæ for the conditions found at the melting-point and in solution are practically the same; this similarity is of importance for they are both in the liquid state.

Returning, however, to the conditions found among the elements it can be noted, that just as we found a great variety of temperatures given as the melting-point of the same element, so also do the records show various values of the specific heat for the same material.

Here again the experimental results point to the existence of a great variety of physical conditions.

But chemistry possibly offers a solution of this question as it recognizes that the element often appears in combinations under multiple or submultiple mass.

Let us distinguish any variable amount of mass present as $m \times 1/2$ atomic weight, wherein m may have such values as 2, 3, or 4, etc. It is proposed to examine the conditions that must result, under the changes prescribed by our formula, when this term appears in the denominator. Our formula becomes then:

$$\text{Specific heat} = \frac{n \times 2.6323\ \epsilon \times 1.28865}{m\ (1/2 \text{ atomic wgt})}$$

On Table XIX several solutions of this equation are suggested whereby, with given changes in n and m, results are obtained somewhat comparable with these variable values of the specific heats.

Here column 2 gives the selected values of n, column 3 those of m, column 4 the values of $\dfrac{n}{m \times 1/2 \text{ atm. wgt.}}$, and column 5 the specific heats as per formula, for comparison with the experimental values of column 6. Column 7 describes the condition of the element.

It is shown, by these results, that a similar range of values can be obtained under this formula; and that possibly the form of this equation represents the conditions reigning within the molecule, in regard to its relations of mass to volume, or to its density.

Under our methods this would signify that, in each kind of atom the element might be of greater or lesser multiple mass, and of such a density that a variable number of expansions n/m might be required to bring it to its temperature of melting or of vaporization.

We must expect then to find the atoms of one element in different states or densities, thus possibly accounting for the differences in the number of atoms of other bodies with which it can unite at different times.

TABLE XIX.

Comparison of the Specific Heat (*S*) with Calculated Results.

Of the energy of cohesion per units of weight and degree at the melting-point, with various changes in the given formula.

Name	n	m	$\frac{n}{m\ 1/2\ \text{A Wt}}$	Calculated Spec.Ht.	Experimental Spec. Ht.	Substance	Observer
C	1	1	1/6	0.5653	0.4670	Graph.	Weber.
C_2	1	2	1/12	0.2826	0.2733	Diam.	Weber.
C_3	1	3	1/18	0.1884	0.185	Gas Carb.	Kopp.
C_4	1	4	1/24	0.1413	0.1439	Graph. 34°	Weber.
C_3	2	3	1/9	0.3768	0.4454	Graph. 642°	Weber.
I	1	1	1/63.27	0.0536	0.05412		Regnault.
I_3	2	3	1/42.18	0.080412	0.082		Avogadro.
B	1	1	1/5.45	0.622	0.4053	amorph.	Regnault.
B_2	1	2	1/10.9	0.311	0.254	amorph.	Kopp.
B_3	2	3	1/8.175	0.4148	0.4053		Avogadro.
B_5	2	5	1/13.62	0.2433	0.254	amorph.	Kopp.
P	1	1	1/15.48	0.219	0.212	common	Person.
P_3	2	3	1/10.32	0.3286	0.385	common	Avogadro.
P_3	4	3	1/20.64	0.16433	0.16981	Red	Regnault.
S	1	1	1/15.99	0.2121	0.20259		Regnault.
S_3	4	3	1/21.32	0.159	0.163	Rhom.	Kopp.
Cd	1	1	1/56	0.06056	0.5969		Regnault.
Cd_2	3	2	1/84	0.0407	0.0385		Herman.

m represents the number of times the half atomic weight enters the formula.

The Calculations of the Latent Heat of Fusion.

On Table XX the calculations of the latent heats of fusion are given for several elements and a few compounds, for which

TABLE XX.

ENERGY OF COHESION BETWEEN STATIONS MAX. E. AND MIN. E.

Or the period measuring the latent heat of fusion of elements.

$$\text{Energy of L. H. of F} = \frac{n \times 2.6323\ \text{Є} \times 0.28865}{1/2\ \text{At. Wt.}}$$

Name	1/2 At. Wt.	Energy Єalors $n = 1$	1000 Є or calories	Experimental L. H. of F.	Value of n.	Calculated L. H. of F.
Al	13.52	0.0562	56.2	80.		
Sb	59.4	0.01279	12.79	16.	1	12.79
Bi	103.65	0.00595	5.959	12.4	2	11.918
Cd	55.85	0.0136	13.604	13.1	1	13.6
Ga	30.45	0.02495	24.953	19.11	1	24.9
Co	29.68	0.0256	25.6	68.	3	76.8
Cu	31.59	0.024	24.05	43.	2	48.1
Au	98.35	0.00772	7.726	16.2	2	15.55
Ir	96.25	0.00789	7.894	28.	4	31.56
Fe (Wt)	27.96	0.02719	27.19	60.	2	54.38
Pb	103.18	0.00736	7.364	5.4	1	7.36
Mg	12.15	0.0625	62.53	58.	1	62.53
Br	39.88	0.0190	19.052	16.185	1	19.05
Hg	100.	0.00759	7.5981	2.8	1/2	3.79
Ni	29.	0.0258	25.89	68.	3	77.4
Os	95.5	0.00795	7.95	35.	4	31.80
Pd	53.1	0.0143	14.309	36.3	3	43.9
Pt	97.15	0.0078	7.821	27.2	3	23.4
Rh	52.05	0.0145	14.59	52.	4	58.
Ru	51.75	0.0146	14.68	46.	3	43.8
Ag	53.84	0.01411	14.115	24.7	2	28.22
Sn	59.4	0.0127	12.792	14.5	1	14.79
Zn	32.55	0.0234	23.34	22.6	1	23.34
I	63.72	0.0120	12.01	11.7	1	12.01
Col. 1	2	3	4	5	6	7

Period Measuring Latent Heat of Compounds.

H_2O	17.96	0.04230	42.306	80.025	2	84.6
$NaNO_3$	84.885	0.00895	8.951	63.	7	62.3
KNO_3	100.92	0.00752	7.528	47.4	6	45.0
$CaCl_2O$	127.61	0.00594	5.942	18.25	3	17.7
$NaPO_3$	101.83	0.00746	7.461	30.345	4	29.6

experimental results could be found. These values are not received as absolutely correct. That of water is undoubtedly the most reliable.

They are calculated from the period of physical change falling between the Max. E. and Min. E. conditions and at constant temperature as already explained. For the final station we have: Max. E. $= \dfrac{n \times 2.6323\ \text{€} \times 1.28865}{1/2 \text{ At. Wt.}}$ and for the initial station: Min. E. $= \dfrac{2.6323\ \text{€} \times n}{1/2 \text{ At. Wt.}}$. Therefore the difference between these two values covers the energy of physical change between these two stations as:

$$\text{L. H. of Fusion} = \frac{n \times 2.6323\ \text{€} \times 0.28865}{1/2 \text{ At. Wt}}$$

Example for cadmium when $n = 1$, then

$$\text{Energy L. H. of F} = \frac{1 \times 2.6323\ \text{€} \times 0.28865}{55.85} = 0.0136\ \text{€alors.}$$

as 1000 € are the equivalent of 1 calory, then 0.0136 € represents 13.604 calories, and the experimental value = 13.1 cal.

Column 2 of Table XX shows the half atomic weights. Column 3 gives the calculated results in €alors, under the assumption that n is always equal to unity.

Column 4 shows these values increased one thousand fold, or the calculated values given in calories, for the gram values of the chemical formula, but still under the above mentioned condition of n equal to unity.

Column 6 shows the values it would be necessary to give n in order to approach the experimental results of column 5. Ten of these results have n equal to one.

Six call for n equal to two, while several have three and four. Column 7 gives final results that are comparable with those of column 5.

Below are also shown similar results for compounds. Here n has various values ranging from 2 to 7.

Among the results we have the latent heat of fusion of water at 84.6 cals, while the experimental value calls for 80.025.

Summation.

The general situation thus indicated may be described as follows: Two independent conditions can be traced at the

melting point, under atmospheric conditions, for a known interval of physical change has been shown to exist between them.

These are first: When the energy of cohesion of the solid is just balanced to the liquid condition by an expenditure of 2.6323 Є per half atom. This apparently covers the sensible heat of physical change which is due when arriving at this station; it accumulates at the rate of 194.2° of change per $1/n$ part of the half mass.

2d. When under the same internal stress $Z^{mp}/2$ and under an extended interval of change, an expansion to a final volume, or 273 degrees is reached as a full measure of cohesion of the half mass to a homogeneous and gaseous condition. To this point the total expenditure of energy equals 3.39174 Є per half atom.

Here both sensible and latent heat are held, for the difference covered between the two states has been shown to equal the latent heat of fusion.

At the same time the value when taken relatively to the *n*th part of the half mass determines the highest rate of change of the body. This is the specific heat of the solid.

On the other hand, when the cohesion of the body is found at *M P* balanced only to the fluid state, it is capable of change under the lesser or minimum rate.

The condition of the half mass acting can then be distinguished as ionized. It is then negative to the higher or positive condition, which has been developed to the full gaseous state.

As the expansion between these two states is isothermal, the energy due to this difference of condition can be rapidly lost to surrounding bodies. Matter can thus revert from the second condition to the first, or ionized state, when robbed of its latent heat of fusion by an external agent.

The Limit.

Returning once more to Tables XVI and XVII which give the double series of specific heats for these stations, attention is called to the last item on the list. It is marked " The Limit " thereon.

A peculiar situation is presented here by the mathematical values of the formula and by its results at Max. E.

It is reached when the half atomic weight equals 128.865. Under these conditions the specific heat =

$$\frac{2.6323\ \text{€} \times 1.28865}{128.865} = 0.026323\ \text{€}$$

or a submultiple of the atomic heat, under the powers of ten.

Our fundamental units of measure also vary under these powers of ten so that changes in decimals may be simply recurrent periods reproducing similar states.

There are certain peculiarities connected with this condition that are to be found in other parts of this series of atomic weights and specific heats. Therefore, our attention is called to the situation described.

The Inert Gases.

The experimental value of the atomic heat was originally determined from the constant product of the atomic weight into the specific heats.

Under our methods, on the contrary, we first derived the constant, which we found as the necessary amount of energy to be supplied to each half atom at the melting-point to balance the cohesion and to bring our original stress Y to zero.

While there may be some doubt as to the true value of our constant, any variation thereof can not alter the relative values of these specific heats, for a double mass will still have its specific heat one half of that of the single mass, and its relation to the full value of the constant will not be changed.

Now, while all these specific heats, as $\frac{\text{Constant}}{1/2\ \text{At. Wt.}}$ are factors of the value of this constant, we can still distinguish among them some that present very simple relations towards that unit. This condition can be readily marked when in addition thereto, a series of factors so related distinguish a distinct class of bodies, as for instance the inert gases.

These inert gases possibly mark the beginnings of certain periodic changes, and He, Ne and Ar, with atomic weights respectively at 2, 10 and 20 naturally bring their specific heats to certain values as simple factors, under the powers of ten. For instance:

He @ 1.695
Ne @ 0.3391
Ar @ 0.1695

This condition becomes marked, when we note that not only the result at the " Limit " 128.86, but at Xenon with one half this atomic weight (64), and krypton with 1/3 of the same (41) share this peculiarity to a certain extent. Two of these elements are also well known inert gases. The specific heats of the trio are as follows:

Kr @ 0.08272
Xn @ 0.05299
" Limit " @ 0.026323

As the specific heats decrease throughout this whole series, with increasing atomic weights, we arrive finally at values representing submultiples of our lesser constant, 2.6323, just as in the earlier ones we had submultiples of the greater one, 3.39174.

As these constants represent certain physical conditions, we apparently are reaching states where the smallest quota of energy possible is required, per degree of change and per *n*.

Hence our term the " Limit."

Again, in this latter station, we are reaching the neighborhood of those bodies, with high atomic weights, that are possessed of radio-activity, or of the bodies which, under atmospheric conditions, cannot retain all the energy they are entitled to.

The question suggests itself: Is the limit, which we have noted related thereto?

At 128.86 certainly the condition of Max. E. or of the specific heat, represents here only a submultiple of Min. E. under the powers of ten. As the former condition holds the latent energy, or energy of the gaseous state representing the latent heat of fusion, this latter can be lost, or dissipated, and the resulting condition would leave the half atom ionized to such an extent at *M P* that it could no longer be rated as an atom, its charge being below the normal or Min. E. In its place, however, it would possess a certain limited amount of affinity, or of returning cohesion.

Hence it would resupply itself at the expense of its surroundings, if the conditions were favorable, or if matter were present in the superheated state. It would then regain its full state of gaseous expansion, or its latent heat of fusion.

Thus it could first lose energy, and then recoup itself, if the surrounding conditions were favorable. For, after first radiat-

ing its free charge of latent heat of fusion and falling below the minimum condition of the atom, it tends to dissipate itself, even to the melting-point.

When after contact with surrounding bodies in the atmosphere, it can recoup this vital charge, it may resume its atomic condition by reaching a minimum condition at Max. E.

This renewal of energy could be furnished by electrical disturbances of the atmosphere, for this phenomenon is an evidence of the withdrawal of energy by physical change from conditions that were previously balanced.

But we can consider this question from another point of view. We have already discussed the conditions of change in the struggle of cohesion vs. heat, when beginning at absolute zero. Here the energy held by the body is a maximum, as the energy of heat is zero. Then, under change to every station, the energy of heat accruing just balances that of cohesion overcome.

We have also sought to prove, from comparisons with experimental evidence, that the energy developed in each volume of change, must correspond exactly to the development of internal energy within n parts of matter, representing the unit or chemical mass.

While other arguments, in this direction, will be offered later, it is sought, at this time, to point out some of the consequences of these claims, for apparently they are germain to the question we have just discussed.

For our present purposes it will be necessary to point out how this particular condition can result, and why it is especially the energy of cohesion of the unit mass that is thus balanced as that of the combining parts.

On this account we shall endeavor to adapt the usual formula for cohesion to the proof that these conditions must result.

We can write: Energy of cohesion $= \frac{M^2}{r}$ where M refers to the mass acting, while r relates to the distance between the centers of gravity of the two half masses, or of the two similar masses M. Their action upon each other is thus limited by the value of r.

But in the particular conditions we are discussing r has a distinct value. It is the natural limit resulting from their

mutual attraction, thus expressing their natural density, or their relation of mass to volume. Under change then r must increase with expansion.

As the energy of cohesion, held by the body, is a maximum at absolute zero, while that of heat is zero, they are evidently developed, under change, in different directions. One increases by rising temperature while the other decreases; hence their relations must be expressed indirectly. The conditions we are discussing can be covered by the following equation:

Heat energy = 1 vol. expansion = energy of cohesion, or

$$\frac{r}{M^2} = \frac{1/2}{M^2}.$$

Now it is urged that this equation covers the precise situation described and indicates under what conditions the two half masses will occupy the unit volume. For, with homogeneous matter, when the distance between the centers of gravity of the two half masses r equals one half, the volume containing the full mass must evidently be unity.

It is thus possible to express, at the same time, the conditions necessary for the development of both sets of forces, *i.e.*, we can cover the determination of the half masses and the natural density of the reagent, expressing its relation of mass to volume. Thus the condition described is a normal one.

1st. In determining unity as the cubic millimeter, centimeter or decimeter we specify a particular molecular weight, a particular mass held by the unit volume, as well as the heat unit measuring the development under change.

2d. We determine also the value of the volume of the expansion in the equation, under these unit measures. For, when representing the natural density, the atomic volumes solid, the volumes of the normal solution, or the gaseous volumes under atmospheric pressure, are each known to represent the internal energy of the chemical unit mass in various conditions.

Thus our formula determines just the relations required to establish the equality between the two sets of forces.

Therefore it is urged that our problem is proved under generalizations that are universally recognized.

The conditions of the gaseous mass may also be represented, as an intermediate state, by the approximate values of n found

at the boiling-point. Here expansion is arrested because the temperature cannot rise higher under atmospheric conditions, though we have shown that some full volume n is required to measure the total cohesion existing within the full mass.

Some of the conditions of this change can be shown as follows, if we estimate the amount of work to be done in separating the two acting parts to a given distance.

Let us call the initial distance between them d and the final one D. Then the distance traversed during the change will be $(D-d)$.

The work of separation is equal to the product of the mean force acting through this distance.

As the initial attraction, under Newton's law, is $\frac{M^2}{d^2}$ and the final one $\frac{M^2}{D^2}$ the (geometric) mean attraction is $\frac{M^2}{Dd}$.

The product of our two terms, or the energy of change

$$= \frac{M^2\,(D-d)}{D\,d} = M^2\left(\frac{1}{d}-\frac{1}{D}\right)$$

If we now separate these two parts until the distance D becomes $2\,d$, the energy of change will add fifty per cent. to the amount originally held.

If we choose the initial d as determining some unit volume of gaseous expansion, and represent by n some particular serial growth, as suggested, we have the change expressed as that of a gas taken in some multiple condition.

At the same time we know that all gases expand equally under a unit of change and, under known conditions, have equal thermal capacities. We have therefore a convenient energy unit for these measurements.

Naturally each of the states measured by these increments, as described, are units of cohesion and must be fairly permanent in character. We know their systems can always reform after cooling, notwithstanding that their energy of cohesion has been balanced by heat to the point of dispersion.

The total expansion necessary for each, however, will vary according to the configuration of the material, as can be seen approximately upon our Chart E.

Possibly, however, n can be composed of two factors, for we find thereon the following changes of volume:

1 Vol. of expansion for Na, K, Cl, Br, I.

2 Vols. of expansion for 1 part of matter in Mg, Zn, Cd, Hg, S, Se.

1 Vol. of expansion for 2 parts of matter in O.

3 Vols. of expansion for 1 part of matter as in Sb, Bi.

1 Vol. of expansion for 3 parts of matter as in N, P.

4 Vols. of expansion for 1 part of matter as in Sn, Pb, etc.

But another condition may apparently occur when the formation of the unit mass is not absolutely permanent.

Possibly under conditions of increasing atomic weights, by the accumulation of ultimate particles like those mentioned above, some limit may be reached eventually which just invalidates our equation, when expressed for n parts of matter.

$$\text{Energy } n \text{ Vols. expansion} = \text{Energy of Cohesion } \frac{n}{M^2}$$

A limit may then have been reached where, the absolute dimensions of particles are such that, under atmospheric conditions and when possessed of its latent heat, the unit mass just exceeds the distance and limit r as described.

The system would then dissipate permanently in gas form, unless restrained in some way, for it is not possessed of sufficient cohesion to hold together. If restrained and upon cooling, with the loss of its latent heat under constant pressure, the volume would be reduced without change of temperature. Then under favorable circumstances cohesion would act again.

This condition might then describe the limit to be reached by the line of increasing unit weights as accumulations of ultimate particles under cohesion.

Returning now to the main argument we have the point emphasized, in any case, that, at stated periods along the line of the atomic weights, the energy held, per units of weight and degree, is a simple factor of either the greater or the lesser atomic heat. In this case it is the inert gases that fall into line, but, at other ratios others probably must do so likewise.

In the heats of dilution we shall see that the tendency, in exchange, is to replace the whole atomic heat.

Hence when we measure the matter present by weight, and the energy acting by the specific heat, we must realize that some factor n is required to determine the energy of the unit mass, or of the parts cohering.

Then between these periodic stations held by the inert gases, we can arrive at intermediate ones, where these factors are divisible by 2 or by 3, etc.

If we call those falling at these intermediate stations dyads or triads, we have a theoretical subdivision suggested.

Evidently then the zeros of these conditions fall, where the inert gases do, not far from the positions held upon the periodic curve by those elements having the greatest atomic volumes, or where the expansion is a maximum in the solid condition.

Naturally, the maximum points fall between these zeros, while others may intervene.

Two Methods of Calculating the Energy of Cohesion.

Thus far in the study of our struggle of cohesion vs. heat we have introduced two methods of calculating the results of the application of our negative stress into volume.

These were suggested by conditions reigning respectively at the melting and boiling-points, and the results served to demonstrate methods for the determination of the latent heats due at these stations, directly in calories.

The methods differ mainly in the determinations of the points of origin of the volumnar growth, owing to the specific resistances to be met with at these stations.

When the origin of volume was located at the melting-point, as the origin of the gaseous expansion, it was understood that the resistance to be overcome was atmospheric or gaseous, and that the cohesion of the liquid state was caused by the external counterstress.

The energy thus developed was called the chemical, in contradistinction to that caused by the solution and dilution of solids. The proof of this statement must be deferred however, until the calculations of the heats of formation can be undertaken.

Our second method relates to the cohesion of the solid and is based upon changes of stress within the volume determining the half atom as the unit of cohesion.

This volume originates at $M\ P^{\circ} - 194.2^{\circ}$.

Under our methods two constants were determined, namely, 2.6323 € and 3.39174 € as atomic heats.

In the calculations of the latent heats of fusion the difference between these constants, when taken as a factor with n

the number of parts acting, was shown to represent values corresponding very closely with experimental results.

Various values of n as n' or n'' are then indicative of specific densities in various materials expressing how many parts or atoms are expanding simultaneously in each per unit volume.

It is proposed to present some evidence to prove that this condition also covers the changes undergone when these materials enter solution, for then these internal stresses disappear. The mass assumes the liquid form, just as it does under the influence of heat. Both changes then correspond to the one calculated.

It can be shown from Thomsen's experiments:

1st. That 2.6323 Є and 3.39174 Є as factors with various values of n represent the heats of solution and dilution of different kinds of mat[illegible]

2d. That each o[illegible]
character:

2.632[illegible]
3.391[illegible]

where the experim[illegible]
ous materials, are[illegible]

The combinatio[illegible]
alluded to certai[illegible]
upon solution an[illegible] as the configuration of the solid disappears.

The Heats of Solution and Dilution.

In order to distinguish between the two methods mentioned by which the energy of change can be produced, we must be careful to select such changes only, in which one of these methods materializes at a time.

During chemical change, however, a transformation of matter must ensue. This test, distinguishing between the two, is then readily recognized, for in solution proper no such change is permissible.

Nevertheless, we can have the material in either of two states, previously mentioned, *i.e.*, at Max. E. or at Min. E.

Each state must have its own specific charge of energy. Then, when the material goes into solution the amount of energy available must indicate which of these conditions has reigned in the earlier solid state.

When the amount determined experimentally corresponds with either of the values we have calculated as the atomic heat of these respective conditions, it is evident that we have identified the source of the energy freed, and that we have a proof of the position regarding the method.

In Thomsen's experiments upon the heats of solution and of dilution he recognizes two coefficients that recall distinctly those we have been discussing as the constants of the atomic heats, the greater and the lesser, namely, 2.6323 Calors and 3.39174 Calors.

These we calculated as expressing conditions found at the melting-point.

In volume three of his " Untersuchungen " on page 211 he records the experimental differences found between the heats of analogous salts, under the following formula:

R	$(R^2 SO^4 aq) - (R^2N^2O^6 aq)$.
K	10,660 cals
Na	10,550 "
Tl	10,660 "
NH^4	10,270 "
	4) 42,150 total
taking *n* equal to	4) 10,527 the average value

2,632 cals as an atomic heat under gram values. But, if we divide by 1000 to reduce calories to Calors, there remains a constant of similar value to the one we have called the minimum atomic heat.

This indicates possibly that these alkaline bodies, as representatives of the positive condition, combine under the lesser form of our constants; an explanation which corresponds with our earlier results. In this way also the well known evidences of traces of cohesion of the liquid still possessed by these bodies in solution could be accounted for.

We find, however, certain quite voluminous data given by Thomsen on this same page relating to the other side of our question. Here he gives the differences between the heats of solution of haloid salts of various pairs of chemically analogous metals. They show distinct relationship to our other constant in the form of 3,200 *n* cals, where *n* varies from two to seven.

This constant again appears in several groups of differences which can be expressed in the form of

$$(S.\ \mathrm{aq}) - (S'.\ \mathrm{aq})$$

where S and S' represent certain changes in the chlorides of Mg, Ca, Sr, Ba and others.

These data are also given in Muir's Thermal Chemistry, page 150. In this case the value of the constant varies from 3003 cals to 3645 cals in 14 cases, while that of n ranges from 1 to 2 and from 18 to 30.

Thus while abundant testimony exists of the recognition of these constants in experimental chemistry, the real question interesting us is, "How far can our methods explain them satisfactorily?"

As stated, they represent first, as Min. E. the rate in Calors under which the energy of heat, as a product of the average stress and volume of expansion, must accumulate to overcome the cohesion of the half atomic weight when expressed in milligrams at the melting-point.

For this purpose the expansion, or change, must continue through an interval of 193.03° A C as a known function of the unit gaseous volume of expansion of 273°.

This relation we have determined from certain mathematical expressions covering the relations of the energies of heat and cohesion.

Secondly, the greater constant Max. E. covers the additional expansion from the melting-point to a certain station situated at 273 degrees from the zero of stress, thus covering the additional energy required to bring this mass to the gaseous state, under one volume of expansion, from the same point of origin to the melting-point.

We have thus a full measure of the constant energy of the half mass in all cases. It can be noted that this latter period covers that required for the completion of the latent heat of fusion of the said mass, for the energy of expansion to the full volume of 273 degrees has been shown to measure that of the cohesion originally held.

As both stress and volume increase directly with the change of temperature through this fixed period, when Max. E. is divided by the value of the half mass, in each case, we find the specific heat that must be active through these changes.

Thus each constant covers specific changes that are common to all material, and offers some aid towards a clearer understanding of the experimental situation.

Seen from our point of view, these applications of our constants to Thomsen's experiments, suggests a solution of another question, they even showing an unsuspected relationship to our greater unit of a third constant given in these experiments.

This reference relates to Thomsen's formulæ for the heats of dilution of the liquid hydrate H_2SO_4 and of the acid HNO_3. To present the results of his determinations of the heats of dilution, Thomsen gives two charts as well as the empirical formulæ of the curves shown, when represented by the values of the ordinates. These latter are:

$$Y = \frac{n \times 17.860}{n + 1.7983} \text{ for the liquid hydrate,}$$

$$Y = \frac{n \times 8.974}{n + 1.734} \text{ for nitric acid.}$$

Here n represents, in the values along the abscissa, the number of full molecules of water for each dilution of one molecule of the reagent. Y, as the ordinate, shows the gram units of heat evolved in each case.*

It is proposed to derive two similar formulæ, that will approximate the same values of Y and will explain the differences found. The results will be expressed in Calors, owing to the different values of the masses in question, while n must necessarily refer to the number of half molecules acting, instead of whole molecules. The introduction of the new values will constitute the changes to be undertaken in the original formulæ.

As the formulæ are each composed of three parts, the numerators, the denominators and the result, we can discuss them in turn.

The Changes Required in the Formula.

When the rate of storage of energy is measured under the half molecular weight, during dilution.

For the present let us confine our attention to the conditions covered under the formula for the liquid hydrate.

*These charts are given in Thomsen's Untersuchungen, volume three, plate 1.

As a factor in this calculation, we naturally have first the numerator of our fraction. This indicates the rate per degree of change at which the energy of heat is balancing that of cohesion per half milligram molecule of the diluent.

As the 1/2 milligram molecule of water, which thus becomes our unit, is $\frac{17.96}{2}$ mgs. of which two are present upon each occasion, and as each added increment of water also consists of two parts, or of $2\,n$, the energy bound under our units, at the rate of one Calor per degree of change, equals

$$2\,n \times 2\,\frac{17.96}{2} \times 1 \text{ Calor.}$$

This equals $2\,n \times 17.96$ C and represents the total original charge.

Secondly, we have the denominator, which implies the rate per degree of change, at which the same balance of energy is maintained, in each 1/2 unit mass of the new solution, or after $2\,n$ parts of water have been brought together with 1/2 molecule of the hydrate.

Each 1/2 unit mass of the solution will consist of $2\,n$ parts of water @ 1 C, and the half molecule of H_2SO_4, the latter holding 3.39174 Calors. Then in this new state, or in the solution, $2\,n \times 1$ C $+ 3.39174$ C will balance, per degree of change, in each half unit mass, as the final condition.

We have thus expressed the original charge of energy, and the final charge, per degree of change, and our answer must be the result of this dilution, or the relation of these terms.

Then: How many 1/2 atomic charges, per degree of change, can be produced from the original quota, when combined at the new rate?

The answer will be given by the quotient.

$$\frac{\text{Original charge}}{\text{Final charge}} = \frac{2\,n \times 17.96 \text{ C}}{2\,n \times 1 \text{ C} + 3.39174 \text{ C}} = Y,$$ or equal to the number of charges present under one degree of change, or again under the specific heat of the solution.

But this final charge, in each solution, will have a slightly different specific heat located somewhere below unity.

If we approximate this value at 1 Calor, we shall be slightly above the true value.

The following table gives the comparative results from Thomsen's experiments and from our high estimate.

n	$2n$	Observed results.	Calculated results.	Differences.
1	2	6,374 cals.	6.4238 Calors	0.044
2	4	9,418 "	9.719 "	0.301
3	6	11,137 "	11.484 "	0.347
5	10	13,108 "	13.412 "	0.304
9	18	14,952 "	15.113 "	0.161
19	38	16,256 "	16.488 "	0.232
1599	3198	17.857 "	17.941 "	0.084

Our values are naturally the one thousandth part of the gram calory.

These values show that when $n = 1599$ sufficient energy has been gradually freed to equal that of a mass of 17.96 mgs. under a specific heat that is practically unity. This really specifies the rate of change of water.

Here then, the hydrate atom has taken the place of one water atom, and henceforth, or when greater amounts of water are added, the new mass must change at the rate of 1 Calor per degree, or as water does. The earlier changes, as indicated by the increasing values of $2\,n\,\text{€}$ in connection with the constant 3.39174 €, in the equation, have been approximating this result.

The conditions, however, have been expressed under slight gradual changes in the specific heats of the various solutions, until eventually this status was reached.

If we turn now to the formula for the heats of dilution of nitric acid, we find that eventually, in this combination, the half molecule of acid tends to replace the half molecule of water, instead of the full molecule as in the last case.

Therefore the maximum heat development will be only about one half that freed by the hydrate.

Thomsen's formula is $\dot{Y} = \dfrac{n\times 8.974}{n+1.737}$

Under our methods this should read:

$$Y = \frac{2\,n\times 1/2\ (17.96)\ \text{€}}{2\,n\times 1\ \text{€}+3.39174\ \text{€}} = \frac{n\times 17.96}{2\,n\ \text{€}+3.39174\ \text{€}} = \frac{\text{Original charge}}{\text{Final charge}}$$

Y then expresses the number of atoms the original charge wil furnish at the final rate, for every degree of change.

From the experiments we see the limit towards which the efforts tend. At this limit the specific heat of the solution is practically unity. Under a dilution of 320 full molecules of water Y reaches only the value of 7,493, while it is evident that under still greater dilution it can eventually reach $\frac{17.96}{2}$, when the acid would replace the half molecule water.

A comparison of the results of this formula with those observed by Thomsen's is given below. It can be noted that, like the earlier one, the correspondence is close, provided we bear in mind that the calculated results are understood to be estimated at too high a rate, in assuming the specific heat of each solution to be unity.

RESULTS OF THE CHANGED FORMULA.

For the dilution of nitric acid.

n	Observed results. cals.	Calculated results. Calors.	Differences.
0.5	2,005	2.0445	0.0395
1.	3,285	3.331	0.046
1.5	4,160	4.241	0.054
2.5	5,276	5.3505	0.074
3.	5,710	5.736	0.026
5.	6,665	6.7006	0.0356

In this second case, then, the constant 3.39174 C represents the atomic heat of the acid when it enters into solution, just as much as it does in the situation found at the melting-point.

The energy which is covered by this development, must be that which is due when $M\ P$ becomes the final station.

It is therefore the energy of cohesion which has been overcome to a fixed limit, the origin of liquidity. Hence it is the cohesion of the solid condition.

It is evident, then, that both the constants under discussion have distinct values, and that they measure the physical changes resulting in solution and dilution.

SIMILARITIES OF CONDITION.

We have examined some of the consequences of the constant atomic stress which occurs at the melting-point. The melting point itself varies for each kind of matter, but the atomic stress found there is constant.

We have also examined the variable stress $-Z^{bp}$ when compared with the constant atmospheric pressure. This variability was indicated roughly upon the chart of "Stress and Volume by Groups."

There is, however, certain other evidence to some extent corroborative of this latter change.

It is shown on Table XXI and Chart G.

In column 10 on Table XXI are given the values of $-Z^{bp}$ for a number of substances that are recorded in column 1.

Of these N, CO, NO have $-Z^{bp}$ very close to eight.

Eight others, however, fall very near to -10, while still others run up to -20 or -25. Those with the condition $-Z^{bp}$ equal to ten are charted upon the lower half of sheet XX.

This shows that even under a great variety of melting-points simple conditions may exist, when the various boiling-points fall at a constant interval of change, from the zero of stress Z°. This interval is closely 262.4 degrees. Among the bodies so shown are Br, I, SO_2, Cl, HCl, and others. Their simple lines of stress are given.

We can also turn to similar data relating to the critical temperature shown upon the same table and chart.

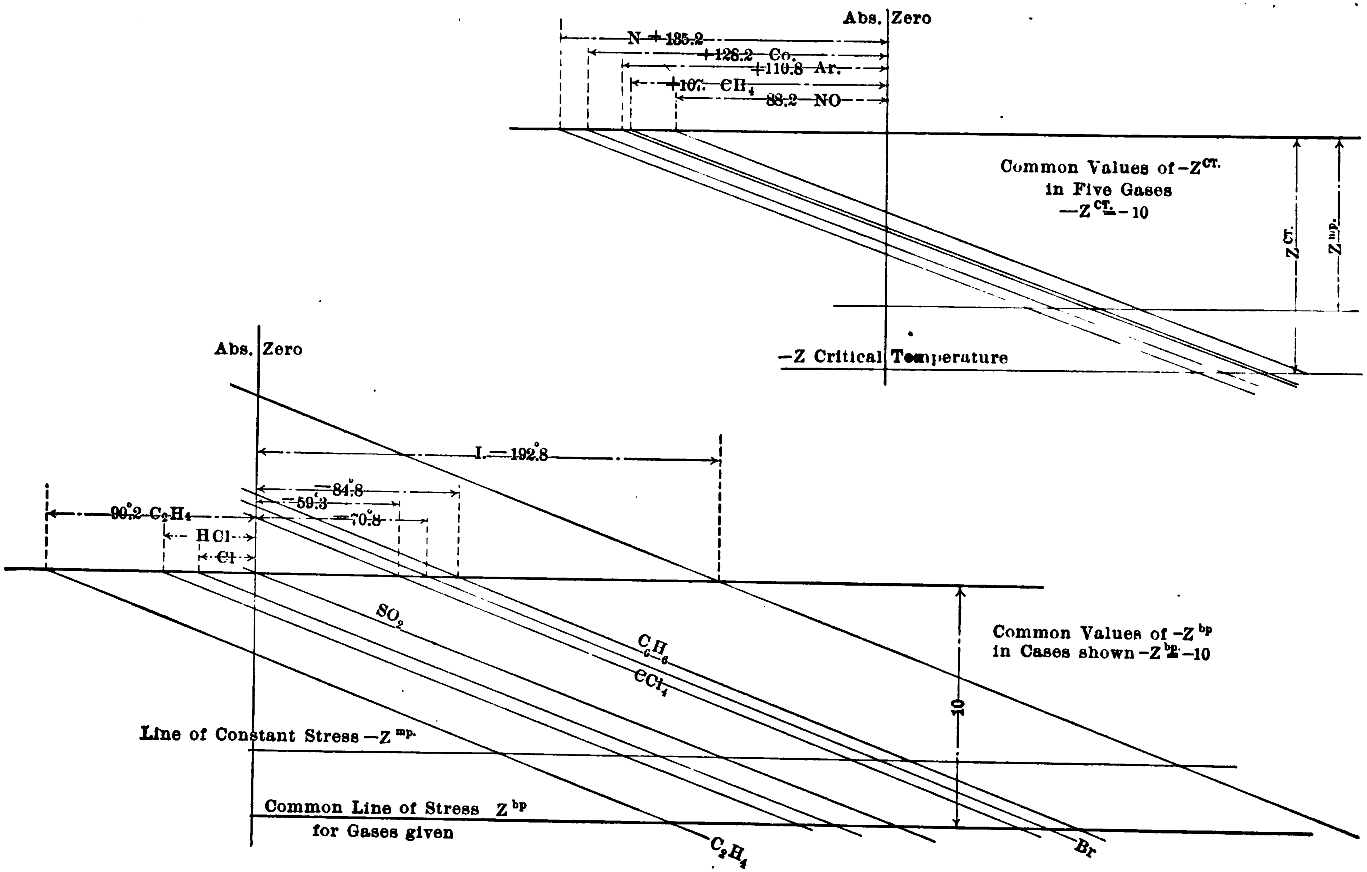
These values are recorded in column 7 of the table; N, CO, NO, Ar and CH_4 have $-Z^{ct}$ very nearly at 10. Others run to 16.67, 20, 130, 150, etc.

These stations of critical temperature are determined as temperatures where, under compression and cooling, the meniscus appears as the first trace of returning cohesion.

Apparently then, this is an indication of the vaporous form occurring under certain critical pressures.

The station is at this time independent of the atmospheric pressure.

From our point of view, these stations are the lowest temperatures determining an interval of change from, either the zero of stress $-Z^{\circ}$, or from the melting-point, in which interval the energy necessary to allow the matter to liquify, can be produced under compression. If, then, this amount of energy



Abs. Zero
N +185.2
+126.2 Co.
+110.8 Ar.
+107. CH4
88.2 NO
Common Values of -Z CT.
in Five Gases
-Z CT. = -10
Z CT.
Z mp.
-Z Critical Temperature
Abs. Zero
I. -192.8
-84.8
-59.3
-70.8
90.2 C2H4
HCl
Cl
SO2
C6H6
CCl4
Common Values of -Z bp
in Cases shown -Z bp = -10
10
Line of Constant Stress -Z mp.
Common Line of Stress Z bp
for Gases given
C2H4
Br

CHART G.

is not produced by compression before the melting-point is reached, the gas cannot liquify.

As stated, this interval of change of 262.4 degrees seems to be common to a number of gases.

Liquidity.

Having examined the development of energy throughout the solid condition, we can now progress one step farther and endeavor to measure the limits of the state of aggregation called liquidity and the amount of energy developed therein.

In the following study of the energies of heat and of cohesion, it will be seen that we can approach the melting-point from either of two sides with a similar result, when limited between certain given stations.

These are: 1st. The one we have already considered under rising temperature, where a period of change equal to 194.2° is required to measure the constant atomic heat, 2.6323 € per 1/2 milligram molecule, and where, under the accumulation of the energy of heat, the quota of cohesion is gradually being reduced to the state of Min. E. at the melting-point.

2d. This station can be approached as a final one, from the reverse side under falling temperature, when, under compression, one seeks to compact the gaseous particles sufficiently to recognize the earliest visible traces of cohesion.

This brings us to the critical temperature, which now becomes the initial station. Here under compression the vaporous condition ends and the liquid begins. Our two stations then mark the two limits of liquidity.

Some evidence can be presented to show that often, in monads, just the equivalent of the atomic heat must be returned to the system between these two stations. In more complex cases, however, some multiple part thereof seems to be required.

On our Table XXI it was shown that the critical temperature often lies at some multiple part of a period of 262.4° from the zero of stress, which falls at a fixed station when taken relatively to the melting-point.

This relation was shown on the table by the relative values of $-Z^{ct}$ when its value fell at -10, -20, -25, etc.

For as the values of $-Z$ increase directly with the number of degrees of change passed through, these latter must vary in the relations given.

TABLE XXI.

RESULTS FROM FORMULA. $X + 26.24\,Z - a = 0$.

	$a = M\,P° - 194.2°$						$-a = 194.2° - M\,P°$		
N.	—214.	59.	+ 135.2	—146.	127.	— 10.	—194.4	78.	— 8.15
CO.	—207.	66.	+ 128.2	—139.5	133.5	— 9.98	—190.	83.	— 8.04
NO.	—167.	106.	+ 88.2	— 93.5	179.5	— 10.21	—153.6	119.4	— 7.91
Ar.	—189.6	83.4	+ 110.8	—121.	152.	— 10.23	—187.	86.	— 7.50
CH_4	—185.8	87.2	+ 107.	— 99.5	173.5	— 10.67			
C_2H_4	—169.	104.	+ 90.2	— 10.1	283.1	— 14.22	—102.5	170.5	—10.
C_2H_6O	130.	403.	— 208.8	243.6	516.6	— 11.72	78.3	351.3	— 5.43
Cl	—102.	171.	+ 23.2	141.	414.	— 16.67	33.8	239.2	—10.
I.	114.	387.	— 192.8				184.2	457.2	—10.0
Br.	— 8.	265.	— 70.8	302.2	575.2	— 19.23	59.	332.	— 9.96
C_6H_6	6.	279.	— 84.8				80.1	353.1	—10.2
$C\,Cl_4$	— 19.5	253.5	— 59.3	285.3	558.3	— 19.03	77.1	350.	—10.5
SO_2	— 76.1	196.9	— 2.7	161.	434.	— 16.45	— 8.	265.	—10.
HCl	—116.	157.	+ 37.2	51.25	324.2	— 13.78	— 35.	238.	—10.5
H_2O	0.	273.	— 78.8	358.1	631.	— 21.06	100.	373.	—11.2
$CHCl_3$	— 71.	202.	— 7.8	260.	533.	— 20.03	61.	334.	—12.4
S.	110.	383.	— 188.8				440.	713.	—19.9
Cd.	322.	595.	— 400.8				783.	1056.	—25.
Hg.	— 39.	234.	— 39.8				356.	629.	—25.5
Zn.	420.	693.	— 498.8				930.	1203.	—26.8
K.	62.5	335.5	— 141.3				689.	962.	—31.3
Na.	95.6	368.6	— 174.4				742.	1015.	—32.0
Au.	1035.	1308.	—1113.8	4300.	4573.	—131.8			
Fe.	1500.	1773.	—1578.8	5200	5473.	—148.5			
Cols. 1	2	3	4	5	6	7	8	9	10

Column 1 gives the names of substances.
Column 2 gives the freezing points in degrees centigrade.
Column 3 shows these values in degrees absolute.
Column 4 gives the individual value of a in each formula.
Column 5 shows the critical temperatures in degrees centigrade.
Column 6 gives these temperatures in degrees absolute.
Column 7 gives the calculated values of $-Z$ for these latter stations.
Columns 8 and 9 give the temperatures centigrade and absolute for the boiling points.
Column 10 gives the value of $-Z$ for these temperatures.

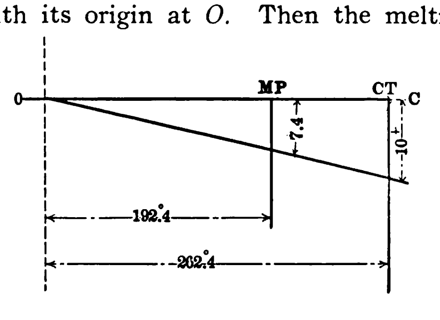
It has been shown by experiment that gas will not liquify unless the station $C\ T$ is reached, either through the expenditure of the energy of compression, or by cooling, or again by the aid of both these agents.

Under the change by cooling the stress of motion $-Z$, due to the temperature reigning, reduces in value with increasing cohesion, or this may be accomplished by the two agents until $-Z^{ct}$ is reached.

It is our purpose to show here that when this occurs the stress $-Z^{ct}$ is still so much higher than $-Z^{mp}$ that the difference accruing between these stations, when developed through a unit volume, will produce just a second quota of 2.6323 €, per part n acting. As we suppose the unit volume to represent the half mass at the melting-point just after the latent heat of fusion is acquired, it is evident that this unit volume is the one we find reigning here.

Hence the new condition originates just where the old one finished. Therefore, the development of this difference of stress, occurring between our two stations, into this unit volume must represent the energy developed per 1/2 unit mass.

This difference of stress can be seen readily from the following chart. Let $O\ C$ be the abscissa on a chart of the atomic stress $-Z$, with its origin at O. Then the melting-point will



fall at 194.2° from this zero, while $C\ T$, for these simple cases, occurs where the stress -10 is reached. This period falls at 262.4° from the point of origin.

Thus the physical change submitted to between these two stations represents the one we are in search of.

The increment of stress $-10-(-7.4) = -2.6$ and when this is developed through the one volume representing the half mass we have $E = 2.6323$ Calors.

Therefore the energy developed through this change by heat in the one sense, or by compression in the other, is just equal to that covered by the atomic heat.

In the latter case, however, the origin of liquidity occurs at the critical temperature as indicated by the appearance of the meniscus, its first symptom. It continues until the melting-point is reached where the whole body is reduced to a liquid. Hence, even in this second direction the same amount of energy must be produced as that occurring during the change from Z° to $M\ P^\circ$ in the other.

On the other hand, if these conditions are not met liquidity does not appear.

The critical temperature can, however, be regarded as the origin of the vaporous condition, just as the boiling point can be distinguished as the origin of liquidity in one sense and that of the vaporous as well.

We have thus located the origin of the vaporous condition both at $B\ P$ and at $C\ T$, although these points are known to fall at different temperatures.

It is evident, however, that they can represent this condition under different circumstances, for $B\ P$ lies at the point of vaporization, when cohesion is being overcome by heat and is disappearing, under atmospheric pressure. The critical temperature, however, lies at the same station, under higher and artificial pressure. This point is arrived at when change is progressing in the reverse direction, and when, under gaseous compression, it is sought to return to the state of liquidity and the first signs of cohesion appear.

Here external energy is being applied to overcome the earlier work of expansion by heat, and the material must naturally pass through conditions reversing the changes found under expansion.

Naturally the same amount of energy must be employed, and the results expressing the energy of compression can, under some conditions, be utilized to measure cohesion, just as we have used heat, under our hypothesis.

Thus a limited method of comparison seems to be offered to test some of our theories.

It is proposed to utilize this opportunity as far as it goes to test our work. It must be understood, however, that this test is applicable only to certain classes of matter, namely, those existing under simple or unit conditions of internal state.

Then, probably, simple laws rule owing to the existence of unit conditions, in contradistinction to more complex ones in other cases, where the proof is more difficult.

One of these unit conditions can be named, however, if we are guided by experimental evidence. This decision confines our test to such material where n equals 1, or where V^{v} is found at the station $M\ P^{\circ}+273^{\circ}$.

As $M\ P$ is always found at 194.2° from the zero of stress, it follows that our proposed comparison is limited to conditions where V^{v} is constant, when measured from the zero of stress Z° as an initial station. The interval to V^{v} as final station is then measured by $194.2^{\circ}+273^{\circ} = 467.2^{\circ}$. This value we specify, for our present purposes as constant A.

Our proposition is then reduced to a new form and under it, an attempt will be made to measure the energy of the gaseous compression of some gases, and to compare it with the energy developed in others by heat, in the same interval, under the condition that the value A is constant.

This condition really implies that the charts of stress shall be similar when we compare them from the origin of stress Z°, instead of from the absolute zero of temperature.

Two such charts are shown marked Chart H. The list of experimental results to be employed is also given on Table XXII.

These charts are shown between parallel lines, station Z° falling upon the one while V^{v} falls upon the other.

Then the points $M\ P$ and $M\ P'$ must also correspond, as the interval 194.2° from Z° is common to both.

It will be seen from the results on Table XXII that $C\ T$ will lie very closely under $B\ P$, just as Z°, $M\ P^{\circ}$, and V^{v} lie under their corresponding points.

These results are shown in two groups comparing the interval $V^v - C\,T$, in the one case, with $V^v - B\,P$ in the other, both therefore covering the intervals of change, described above. The point we hope to prove must follow the acceptance of their equality.

In the cases cited the points $C\,T$ of one group all fall at

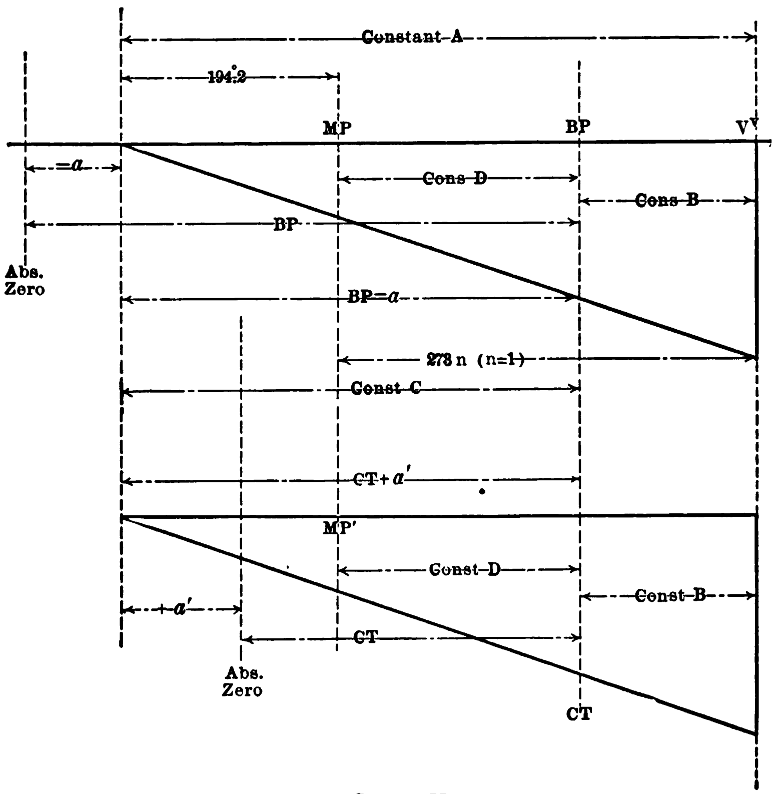


CHART H.

fairly similar intervals from Z° and V^v just as the points $B\,P$ do in the other group, as will be seen from the results shown in columns 9, 10, 11, and 12.

Then $C\,T + a' = B\,P - a$ or constant C.

$V^v - C\,T = V^v - B\,P$ or constant B.

It will be seen that the intervals $V^v - C\,T$ and $V^v - B\,P$

TABLE XXII.

$$x + 26.24\,Z - a = 0$$
$$\log 26.24 = 1.4189678$$

Name	Abs. Freezing Point.	$-a$	Crit. temp.	$-Z^{ct}$	Abs. BP	$-Z^{bp}$	$V^{V} = FP + 273n$	n	Const. C $a' + ct$	Const. B $v^{V} - ct$	Const. C $Bp - a$	Const. B $V^{V} - Bp$	Const. A = 194.2° + 273n
N	59.	+135.2	127.	—10.	78.5	— 8.75	332.	1	262.2	205.			467.2
CO	66.	+128.2	133.5	— 9.981	83.	— 8.047	339.	1	261.7	205.5			467.2
NO	106.	+ 88.2	179.5	—10.21	119.4	— 7.918	379.	1	267.7	199.5			467.2
Ar	83.4	+110.8	152.	—10.23	86.	— 7.506	356.4	1	262.8	204.4			467.2
CH_4	87.2	+107.	173.5	—10.67			360.	1	280.5	186.7			467.2
C_2H_4	104.	+ 90.2	283.1	—14.22	170.5	—10.	377.	1			260.7	206.5	467.2
Cl	171.	+ 23.2	414.	—16.67	239.2	—10.	444.	1			262.2	204.8	467.2
I	387.	—192.8			457.2	—10.08	660.	1			264.4	202.8	467.2
Br	265.	— 70.8	575.2	—19.238	332.	— 9.96	538.	1			261.2	206.	467.2
SO_2	196.9	— 2.7	434.	—16.45	265.	—10.	469.9	1			262.3	204.9	467.2
HCl	157.	+ 37.2	324.2	—13.78	238.	—10.5	430.	1			275.2	192.	467.2
C_6H_6	279.	— 84.8			353.1	—10.23	825.	2			268.2	472.	740.2
S	383.	—188.8			713.	—19.99	934.	2			524.2	221.	745.2
Col.	1	2	3	4	5	6	7	8	9	10	11	12	13

The charts are located so that the zeros of stress correspond.
Then in certain cases $C\,T + a' = B\,p - a =$ Const. C.

$$V^{V} - B\,P = V^{V} - C\,T = \text{Const. B.}$$

which we have called constants, while varying somewhat, average about 200°.

Owing to this approach to constancy the question arises: Are we justified in concluding that they cover precisely the same physical change?

In the latter case, we have determined that under gaseous expansion this interval $V^v - B\ P$ covers the development of the latent heat of vaporization, or the energy necessary to carry the material from $B\ P$ as vapor to V^v as gas. In the former case we have the reverse change, for, under stated conditions, it covers the energy required to bring the gas from atmospheric conditions at V^v to that station where the vaporous ends in the formation of the meniscus at the origin of liquidity. Under the energy developed during these equal intervals, it would seem that the external energy was simply reversing the work done by heat.

At the same time, these intervals can only be determined through the use of our two hypothetical stations $Z°$ and V^v.

These are the initial and final stations of our chart and they determine our factors of atomic stress and volume.

If, then, our question can be answered in the affirmative, some evidence will have been presented supporting the existence of these stations.

An Adaptation

Of the Theory of the Antagonism of the Energies of Cohesion and Heat to an Estimate of some Heats of Formation.

The purpose of this chapter is to outline a method in which various data in our possession can be combined to estimate the heats of formation. An attempt will be made to fix the limits within which this energy must be developed.

In order to accomplish our purpose, we must be able to approximate the amounts of energy held in both the reagents and the product. The first will represent the amounts to be disposed of, and the latter the amounts rebound. The difference will be the value sought.

If, however, there is more energy bound than is supplied by the reagents, the heat of formation ($H\ F$) will be negative.

In order, then, to simplify matters as much as possible, it will be advisable to select reactions where the number of reagents participating are a minimum.

We are limited also in our selection by the fact that we must know the melting and boiling points of both reagents and product, in order to make the experiment available for our purposes. With a knowledge of these factors, the energy freed can be determined and compared with experimental results. Then also the values of our coefficient B can be determined, and its approach to the theoretical value of 1000 estimated.

Hitherto we have succeeded in expressing the energy of the unit mass when the two half atoms were of equal weight.

It was calculated as that of some gaseous volume of expansion developed to a known temperature V^v. We were thus able to represent the energy controlling the internal condition of the element itself.

The unit mass was thus brought to the limit of the chemical volume contained in n volumes at the above mentioned station $M\ P+273\ n$.

The energy of this expansion thus becomes a measure of that of cohesion of the given mass in its original state.

At the same time the given weight in milligrams, the given temperature and the value n expressing the volumes in cubic millimeters defines the internal situation completely, for the relation of mass to volume specifies the reigning density.

Naturally when the mating half atoms are no longer equal the cohesive effort holding them together varies from the given value of n at the same temperature. It must represent that of the new conditions. If n originally had been 1 under different combinations it could now become 1/2 or 2 at the same station.

Thus by the internal attributes of a different density the change in cohesion, caused by the presence of unequal half atoms, could be expressed.

Owing to decisions mentioned earlier in this paper it is thought advisable to place the initial station of the gaseous expansion at the melting-point. The energy of the solid condition, or that developed before this station is reached, must have been partly disposed of by the act of solution.

We have then, mainly, to account for the energy developed later, under gaseous expansion with the temperatures rising above the melting-point, though possibly some of the heats of dilution may at times still be retained in the normal solution.

They may not as yet have been developed to their full limit, but their state of development can be estimated as already shown.

As the final station we have already mentioned the point V^v. The interval thus determined by our stations represents what we have called the chemical volume under atmospheric pressure. But the expansion from $B\ P$ to V^v we have already recognized as isothermal. Our fractional volume, originally held at $B\ P$, increases to that of the complete unit, as a fixed and common measure of the energy of mass by expansion.

But the temperature held at V^v corresponds precisely with $B\ P$, as the reacting stress is limited by the atmospheric pressure. Hence, while we assume full volumes held at $B\ P$ for the calculation of the stress $-Z$, we must hold that station as the limit of the chemical volume in this respect.

But other points claim our attention.

It is evident that in ordinary chemical reactions, when the reagents in solution are brought into immediate contact, the parts as well as the product acquire a common temperature.

As the temperatures met with at the various boiling-points, representing the respective chemical volumes do not cover this condition, evidently some correction must be provided for. It is essential that this condition be observed in our calculations, and that the process shall be taken as terminated, in each, only after all the energy of cohesion has been measured by heat. If this is not attained, some energy of the constituents would not be correctly estimated.

It is also evident that in the reaction proposed, the temperature of the final station sought cannot coincide with that produced during the experiment. In the latter cohesion acts directly, whereas, under our methods, we must introduce the station expressing its equivalent heat energy.

In order to insure that all the participants in this reaction reach the state prescribed as V^v, we must choose our final station at least as high as the highest boiling-point, whether this be of reagent or of product.

We shall designate this station as t^c, the temperature of calculation.

Naturally all other participants in this reaction must be superheated at t^c, or be charged with heat energy ($H\ E$) in excess of that required to balance the energy of cohesion.

This latter can be designated as atomic energy ($A\ E$).

But the final difference, which represents to us the amount of heat freed, will approximate closely the heats of formation for that particular reaction. In fact, the error could be estimated as the amount required to raise the mass present from laboratory temperature to t^c. For our present purposes, however, this error will be neglected and the calculated results compared directly with the heats of formation.

In the table of results to be submitted later it will be noticed that in cases where the highest boiling point falls below laboratory temperature, that temperature is taken as t^c, with a value of 293° *a. c.*

We have then arrived at the conclusion that, for each material in the coming estimates of heats of formation, our initial and final stations must be taken at $M\ P$ and t^c, regardless of their respective chemical volumes.

We can now designate as the atomic energy ($A\ E$) all that energy possessed by the material in solution, which will be measured by the exhaustive physical change from $M\ P$ to V^v, the latter being an intermediate station between $M\ P$ and t^c. This interval represents what we have called the chemical volume.

Any energy acquired between the station V^v and our final station t^c, can be designated as heat energy ($H\ E$).

Then the total chemical energy ($C\ E$) for any one of the participants can be written:

$$C\ E = A\ E + H\ E.$$

By $C\ E\ (c)$ and $C\ E\ (d)$ we can further denote the respective energies belonging to the reagents, and by $C\ E\ (p)$ that of the product.

Finally, we are able to write the formula of the heats of formation as $C\ E\ (c) + C\ E\ (d) - C\ E\ (p) =$ Result.

We will call this result " Summa $C\ E$ (Calors) " in contradistinction to $H\ F$ (cals), the experimental value of the reaction in question.

Then Coef. $B = \dfrac{H\ F \text{ (cals)}}{\text{Summa } C\ E \text{ (Calors)}}$ with a theoretical value of 1000.

Determination of $C\ E$.

Evidently then the question now resolves itself into a measurement of the chemical energy, in any mass placed under the test,

with t^c limited to a value which is equal to the highest boiling point of any of the constituents, or to laboratory temperature provided t^c falls below that station.

For this purpose we must ascertain the final average stress reigning at t^c and the final volume found at that point, which we can call V^c.

Then $C\ E$ = average stress $t^c \times$ volume V^c, thus including $H\ E$.

If we assume, as before that the final volume found among the elements at $B\ P$ when the latent heats of vaporization has been acquired, equals V^v, or its equivalent, then the total expansion to the new station V^c, which is caused by the summaiton of $H\ E$ to the original atomic energy $A\ E$ can be expressed as:

$$V^c = V^v\left(1 + \frac{t^c - B\ P}{273}\right).$$

All the terms in the last factor are known, therefore, to determine V^c it is only necessary to find the value of V^v, or of its equivalent when the combining half masses are unequal.

As the solving of our main problem, the calculation of $C\ E$ is now narrowed down to the determination of the average stress t^c, and of the volume V^v, or its equivalent, it will be advisable to examine separately the conditions determining the value of each of these factors.

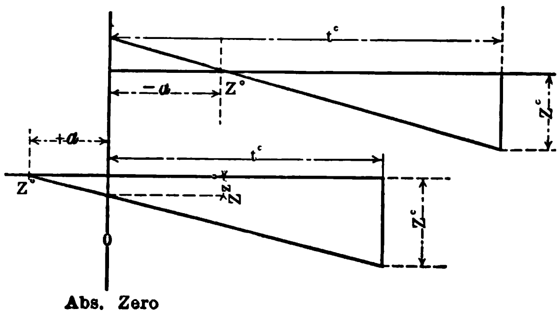
The Calculations of the Average Stress.

We must revert to our original formula.

$X + 26.24\ Z - a = 0$, where X represents the absolute temperature of t^c and $-Z$ the acting stress or pressure resulting therefrom.

Owing to the great range of values, however, that are represented by $-a$, the situation calls for some care. From earlier results, we found $-a = 194.2^\circ - M\ P^\circ$ and recall that when the term $M\ P$ is smaller than 194.2 the formula takes a special form, as $X + 26.24\ Z + a = 0$. This variation divides matter into two classes, as shown on the accompanying sketches.

One part have their zero of stress to the right of absolute zero and the balance have this point falling to the left of that station. We recall that in the calculations of the latent heat of vaporization it was necessary, in the latter case, to discount all stress that might have been acquired before absolute zero was reached.



As the absolute zero is the zero of the motion caused by heat, the increment of stress gained from this station to t^c must be expressed by the difference determined for these stations by our formula. Calling the stress at the final station Z^c, and that at absolute zero Z^z, we have the average resulting, for these cases, at $t^c = \frac{Z^c - Z^z}{2}$.

In contradistinction to this result we have that of the first, or the normal class, as final stress $t^c = \frac{Z^c}{2}$.

These classes are, however, readily distinguished by the sign falling before a in the equation of stress.

It will be noted that the conditions thus described are precisely those used in the calculations of the latent heat of vaporization.

Our general equation now has a double form, as follows:

$$\text{When } a \text{ is positive, } C\,E = \frac{Z^c - Z^z}{2} \times V^c.$$

$$\text{When } a \text{ is negative, } C\,E = \frac{Z^c}{2} \times V^c.$$

To recapitulate: In these calculations of the average stress at t^c, we have called attention to three points, as follows:

1st. That ordinarily, the common temperature t^c, of a reaction, may be taken at the highest boiling-point of the constituents, and that the error of the calculation may be estimated.

2d. That when t^c falls below the ordinary temperatures it must enter the calculations at the value of the laboratory temperature in order to cover the complete energy changes.

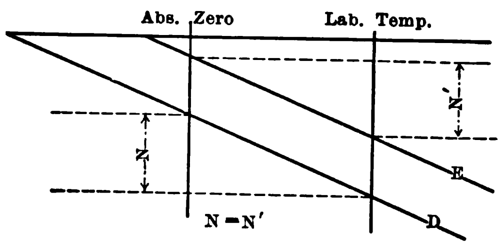
3d. That a change is required in the formula for the final stress, *i.e.*, the subtraction of Z^z when the last term a of the equation becomes positive.

In the set of tables, to be given shortly, presenting the calculations of the heats of formation, each of these cases occurs several times.

The last change occurs in all those reactions where O, H, Cl, H_2S are found, so that it appears, in some form, in the majority of the examples presented.

The substitution of the laboratory temperature occurs in the calculations of H Cl, and N_2O.

A peculiar combination of these two exceptions presents singularly simple results. It can be explained through the use of the following sketch. The situation arises among gases



with low melting-points, where the line of stress intersects the abscissa beyond absolute zero, and where, as stated, the average stress becomes $\frac{Z^c - Z^z}{2}$.

This condition is shown on the lines marked D and E on the adjoining sketch.

Secondly, here also we have located the station t^c at laboratory temperature, with the result that both stations, absolute zero and laboratory temperature, are common to the two stress lines. The differences referred to, in the two cases, are marked N and N' on the sketch; but as the intersecting lines are parallel N must equal N', and the final acting stresses are the same in value. This result can be shown, as follows, from values noted upon Table XXVI, for the calculation of the heats of formation of N_2O.

We have the equation for N as: $X+26.24\,Z+135.2$	$=$	0.
whence with $X = t^c = 293$ (lab. temp.) Z^c	$=$	16.318
X^z @ abs. zero $= 0.$ Z^z	$=$	5.1525
Then $Z^c - Z^z$	$=$	11.1635
The average stress		5.582

* * *

Secondly for O we have $X+26.24\,Z+107.2$	$=$	0.
with $X^z = t^c = 293$ we find Z^c	$=$	15.251
$X^z = 0.$ Z_z	$=$	4.0853
Then $Z^c - Z^z$	$=$	11.1657
The average stress again		5.582

* * *

Lastly for N_2O, or for the product,		
we have the equation $X+26.24\,Z+36.2$	$=$	0.
whence with $X = t^c = 293$, we have Z^c	$=$	12.545
with $X^z = 0.$ Z^z	$=$	1.3795
$Z^c - Z^z$	$=$	11.1655
and again the average stress equal to		5.582

This condition occurs in the calculations of HCl as well as in N_2O.

In these reactions all stresses, for the two pair of reagents and the two products, have the same value,

$$1/2\,N = 5.582 \text{ kilo @ sq. mm.},$$

and still their heats of formation as determined fall at 98.76% and 102.4% respectively of the experimental.

It can also be noted, in favor of our methods, that the determinations of $H\,F$ given in these tables as the chemical energy and derived from the product of stress and volume, as described, are still expressed, directly, in Calors, thus representing the one thousandth part of the calory.

The Determination of the Volume of Vaporization V^v and Its Equivalent Form V^x. Both Representing the Unit Mass as Factors in the Value of V^c.

On our chart E marked " Study of Stress and Volume " our attention was called to the position of the point V^v in relation to that of the boiling-point.

At this point we located the final station, in the calculation of the energy of the unit mass, of the various materials of whose latent heats of vaporization we possessed experimental determinations.

We found it located at $M\ P + 273\ n$, where n represented its value, indicating at the same time how many expansions in volumes of 273°, were necessary to measure the balance of cohesion from the initial station $M\ P$ to complete gasification, under atmospheric pressure.

In our calculations of the latent heat of vaporization this station V^v was proved to symbolize the energy of the unit mass of any matter. Thus we have at this point a relation of $\frac{\text{Mass}}{n \text{ Vols.}}$ indicated, where mass equals unity. Thus a rate of mass to volume is indicated determining a standard density, or a normal condition, in which the gas must exist at V^v as a base, under atmospheric pressure.

But, by the same calculation, we have shown that this condition is to be found at $B\ P$, under this pressure, when the volume held there is submitted to expansion under the energy of the latent heat of vaporization.

In those very cases, however, shown on Chart E only standard conditions are presented, which are to be found among the elements. These particular conditions are covered and governed by the given values of $M\ P$ and $B\ P$ and by the interval included between them.

They are simply those in which two similar half atoms are in combination forming a unit mass, as expressed by the molecular weight. The energy of this combination under cohesion is the energy of the unit mass.

But, in the conditions mentioned above, these parts are similar and the matter resulting is elementary.

From this point of view, we have hitherto always determined V^v as indicating the amount of expansion required to balance the cohesion present to the gaseous state, under atmospheric pressure, with pairs of equal and similar half atoms.

The conditions we are called upon to estimate in the study of the heats of formation differ materially from those just described. They are those existing just prior to the occurrence of a chemical combination, which when completed will be

measured by an interval between new melting and new boiling points. While reacting then, the atom of one element is called upon to unite with another from a foreign system, the original halves forming two parts of the new.

Thus we have a new form of cohesion, or possibly of adhesion, but one where the resultants in stress and volume will certainly differ from those previously held.

Hence the conditions that arise will differ from the original ones and will be covered by new melting and new boiling-points.

It is readily conceivable that the final volume V^v, or the standard density of each reagent as a measure of the new amount of cohesion acting, will assume, while representing the unit mass, some equivalent volume of the older one.

This condition will be determined by the reacting stresses of dissimilar pairs, which are now in presence of each other, as distinguished from the reacting stresses of similar forms and mass, determining the earlier density.

It is necessary, then, that we should determine, for each reagent, some equivalent volume, as a measure of the cohesion existing under the changed conditions.

Each new volume must, as it were, symbolize the unit mass by expressing another rate of $\frac{\text{Mass}}{\text{Vol.}}$ or a density that results from gravitational force, when dissimilar atoms are in presence of each other.

When unlike particles are thus brought together in pairs, under such conditions that movement is possible, action is induced when the half masses of one kind are short of the energy of heat, or are negative, and when the others are relatively superheated or are positive.

The parts are then ionized, the negative ones being possessed of affinity, or of a balance of cohesion.

Under these circumstances more favorable groupings are often possible and changes will occur influenced by the nature of the half masses acting.

We must understand that in the transfer no energy can be lost, each half atom seizes a new mate under the influence of a new affinity, or of new conditions under the gravitational law, which we express by a change from V^v to V^x, indicating that the original half mass is now bound under a new rate of compression.

The energy of expansion of V^x is to cover this rate, with the understanding that the conditions resulting after the change are a complete expression of the energy of cohesion in the matter present. For, with a new volume at V^x a new condition of equilibrium must exist between the half masses now acting. Under change the energy stored can be measured in the usual way.

If the particles are not ionized, but remain neutral, no action occurs. Or again, if the particles are only slightly ionized, so that the reaction occurs slowly, the speed can be influenced by the presence of a third set of atoms.

When the latter, under catalytic action, are able to induce locally greater compression, among the acting parts, the interaction of these pairs is stimulated. But, in uniting they bind only specific amounts of gravitational energy, which are entirely dependent upon their own internal conditions.

On this account they cannot detract in any way from the amount originally held by the third set of particles. These latter act then by their presence only, stimulating the rate of change.

If under any of these conditions action does occur and an excess of energy is present over that required by the new pair, it is freed; or if sufficient energy, for the new condition, is not present a lowering of the temperature of the total mass indicates the shortage.

The amount covering the actual cohesion present is still retained in the material, and it is just that amount we are seeking to measure by the expansion of the material into volumes between fixed stations.

At present we are unable to determine this expansion, or even the conditions of cohesion which it represents, except by the merest outline. We know that this force is related to the acting mass and to the form of the ultimate particle.

This latter attribute determines the original distance apart of these particles, from which they must be driven by expansion to a neutral position under atmospheric pressure.

Eventually, however, a law must be determinable from a knowledge of the heat energy conditioning the change, and of the stresses interacting in the half chemical masses.

For the present we must be satisfied with a tentative deter-

mination. This can be attempted if we assume the conditions specified by our hypothesis to be true.

We can then ask: What volumes are necessary, under this assumption, to represent the energy of change in some of the reactions for which the heats of formation have been determined?

An answer to this question has been essayed, and various volumes assumed under which the calculated energy is comparable with the experimental.

The energy of the new volumes, assumed for the above mentioned change, must still represent that of the unit mass, but from a new condition of cohesion, one which must have a new value for every combination, for in each reaction the relation of the reacting masses varies. Then the energy of cohesion will, in each case, be measured by a different degree of expansion.

If in the element V^v was unity, it may now assume values of 1/2 or 2, or some similar change, each expansion still covering that of the unit mass.

Hence our term of equivalent volume, which it is proposed to designate as V^x expressing this new rate or density.

Then in the fomula for the heats of formation,

$$V^c = V^v\left(1 + \frac{t^c - B\,P}{273}\right)$$

V^x takes the place of V^v on account of the changed conditions.

In order to express the relations of these volumes under the changed density, we can write $V^x = \frac{\text{Specific Wgt. } (H)}{\text{Atomic Wgt.}} \times V^v$, wherein the term specific weight, in terms of hydrogen, represents that part of the atomic weight now held per unit of volume, in contradistinction to that of the exact atomic weight formerly held.

Then V^x, in its relation to V^v, expresses the new rate under which a specific part of the unit mass, or of the atomic weight of a material is bound per unit of expansion.

When $V^x = 2$, we express the fact that, in the material in question, the density, or rate of $\frac{\text{Mass}}{\text{Vol.}}$ is such, that two unit weights of mass are held in the normal volume, or that the

energy of the acting mass can be measured by an expansion through two volumes. The normal unit volume being that found at V^v under atmospheric pressure.

EXPERIMENTAL EVIDENCE.

At this point we must turn again to experimental evidence as a guide in determining the various ranges through which this specific weight (H) can pass. As dissimilar atoms often unite under several conditions, it is evident that our term $\frac{\text{Spec. Wgt. }(H)}{\text{Atom. Wgt.}}$ may have several values, for the numerator may be increased or decreased.

TABLE XXIII.

COMPARISON OF EQUIVALENT VOLUMES. $V^x = V^v \frac{\text{Specific Wgt. }(H)}{\text{AtomicWgt.}}$

On basis of constant mass with variable temperature and constant pressure.

Specific Wgt. (H) = Spec. Gravity (air = 1) $\times$ 14.43.

1	2	3	4	5	6	7	8	9
I.	8.72	185	458	125.8	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.84	250	523	127.6	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.70	447	720	125.6	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.8	250	523	127.	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.8	450	723	127.	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.05	665	938	123.4	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	8.72	1000?	1273?	125.8	126.5	1	1	$V^x = 1\times1/1 = 1.$
I.	5.87	1100?	1373?	84.7	126.5	1	$\frac{84.7}{126.5}$	$1\times0.6695=.6695$
I.	4.76	1500?	1773?	63.7	126.5	1	$\frac{63.5}{126.5}$	$1\times0.5035=.5035$
Br.	5.46	100	373	79.9	80.	1	1	$1=1\times1/1=1.$
Br.	5.38	100	373	77.6	80.	1	1	$1=1\times1/1=1.$
Br.	4.43	1500?	1773?	58.9	80.	1	$\frac{58.9}{80.}$	$1\times0.7362=.7362$
Hg.	7.03	424	697	101.5	200.	2	0.57	$2\times0.57=1.015$
Hg.	6.98	446	719	100.7	200.	2	0.50	$2\times0.5=1.00$
Hg.	6.7	882	1157	96.7	200.	2	0.488	$2\times0.488=0.967$
Hg.	6.96	1000?	1273?	100.4	200.	2	0.52	$2\times0.52=1.00$
Hg.	6.81	1567	1840	98.27	200.	2	0.496	$2\times0.496=0.987$

1	2	3	4	5	6	7	8	9
S.	6.62	524	797	95.5	32.	2	$\frac{95.82}{32}$	$2\times 2.984=5.96$
S.	2.93	665	938	42.3	32.	2	$\frac{42.3}{32}$	$2\times 1.32=2.64$
S.	2.23	860	1133	32.2	32.	2	$\frac{32.2}{32}$	$2\times 1.=2.00$
S.	2.24	1042	1315	32.3	32.	2	$\frac{32.3}{32}$	$2\times 1=2.00$
S.	2.17	1400?	1673?	31.3	32.	2	$\frac{31.3}{32}$	$2\times 1.=2.00$

Column 1 gives the names of substances experimented upon.

Column 2 shows their specific gravity (air = 1) at temperature of observation as recorded in columns 3 and 4. The latter gives the degrees absolute centigrade. Column 5 gives the specific weight (H), while Column 6 shows the atomic weight. Column 7 gives the value of V^{v}.

Column 8 presents the value of the ratio $\frac{\text{Specific Wgt. } (H)}{\text{Atomic Wgt.}}$.

Lastly column 9 contains the calculated value of V^{x} for the particular experiment in question, as a product of V^{v} and the above mentioned ratio.

Hence it will be necessary to distinguish each series of conditions as a range.

Here, again, we must recognize the conflict of cohesion and heat, and realize that the changes met with, through various degrees of temperature, must alter the density by an expenditure of energy, while a corresponding change can also occur in a reverse direction, under the action of cohesion.

In one sense therefore the changes that can be produced by heat can also in another be produced by cohesion.

The energy of heat can still be our measure of change. Many experiments are recorded giving the specific gravity (air = 1) of the elementary gases, at various temperatures.

If we call the specific weight ($H = 1$) equal to the specific gravity (air = 1)$\times$14.43 for a certain temperature, we have this weight under the desired conditions.

Then the values of the specific and atomic weights are commensurable, and the desired values of V^x can be calculated for the temperature of observation.

Several ranges of such results are given in the Tables XXIII and XXIV and recorded upon Chart I.

The experimental results are taken mainly from Muir's Principles of Chemistry,* where their various sources are recorded. A few, however, are taken from results obtained by Prof. Dewar.

TABLE XXIV.

1	2	3	4	5	6	7	8	9
Cl	2.45	200	473	35.36	35.37	1	1	$1\times 1/1=1.$
Cl	2.61	1000?	1273?	37.67	35.37	1	1	$1\times 1/1=1.$
Cl	2.44	1200?	1473?	35.36	35.37	1	1	$1\times 1/1=1.$
Cl	2.21	808	1081	29.08	35.37	1	0.8223	$1\times 0.8223=$ .8223
from	1.85	1028	1305	26.69	35.37	1	0.7547	$1\times 0.7547=$ .7547
$PtCl_2$	1.65	1242	1515	23.81	35.37	1	0.6731	$1\times 0.6731=0.6731$
Cl "	1.66	1392	1665	24.04	35.37	1	0.6797	$1\times 0.6797=0.6797$
Cl "	1.61	1567	1840	23.23	35.37	1	0.6568	$1\times 0.6568=0.6568$
H.	.9655	−252.5	20.5	14.	1.	1	14/1	$1\times 14=14.$
H.	.06949	0	273	1.	1.	1	1.	$1\times 1=1.$
N.	.972	0.	273	13.99	14.	1	$\frac{14}{14}$	$1\times 1=1.$
N.	.9696	−184.	89	14.06	14.	1	$\frac{14.06}{14}$	$1\times 1=1.$
O.	1.1056	0	273	15.96	15.96	1	1	$1\times 1=1.$
O.	1.106	1400?	1673?	15.97	15.96	1	1	$1\times 1=1.$
O.	1.07	1567?	1840?	15.44	15.96	1	1	$1\times 1=1.$
O.	3.4013	*B P*	90.3	49.35	15.96	1	$\frac{49.35}{15.96}$	$1\times 3.09=3.$
Oz	1.658	*B P*		49.35	23.96	1	$\frac{49.35}{23.96}$	$1\times 2.05=2.00$
1	2	3	4	5	6	7	8	9

*Page 33, 2nd. edition.

Variable amounts of cohesion sometime held at the initial station can be indicated by the variations in value, or the range, of the equivalent volume V^x, under degrees of change through heat.

Abs.
Zen.

Iodine	MP	BP	458°	720°	938°	1273°	1373°	1773°
Val. V^x		1	1	1	1	1	0.66	0.5035

Br.	Mp	BP	373°	1773°
Val	V^x		1	0.7362

Hg	MP	BP	697°	719°	1155°	1273°	1840°
Val.	V^x		1	1	0.967	1.	0.987

MP	BP	473°	Chlorine	1273°	1473°
Val.	V^x	1		1.	1.

MP	BP	Cl from $PtCl_2$	1081°	1305°	1515°	1665°	1840°
Val	V^x	(Victor Meyer)	0.822	0.754	0.673	0.679	0.656

MP	Bb	273°	Oxygen	1673°	1840°
3.		1	Val V^x	1	1

MP	154°	Ozone
	2	

Chart I.

Sulphur	MP	BP	797°	938°	1133°	1373°	1673°
Val	V^x		6	2.64	2.	2.	2.

Detailed Results.

From Tables XXIII and XXIV.

Our purpose, in making this comparison, is to show how exactly those values of V^x, which satisfy the conditions of the calculations of the heats of formation, fall within the experimental ranges described.

The details of these calculations will shortly follow, and we can then see how, in some particular reaction, each value of

V^x replaces our standard and normal V^v, when dissimilar atoms come into the presence of each other.

For these changes, when occurring with dissimilar pairs of half atoms, our formula has been given as:

$$V^c = V^x\left(1 + \frac{t^c - B\,P}{273}\right).$$

The experimental results tend to endorse our selection of volumes that have been made tentatively to comply therewith.

On Tables XXIII and XXIV experimental results, with each of the following elements, have been classed independently.

They represent the specific gravities (air = 1) at given temperatures of I, Br, Hg, Cl, Cl from $PtCl_2$, O, Oz, S, H, and N. These values are given in column 2.

Column 1 shows the name of the element experimented upon.

Column 4 gives the temperatures of observation.

Column 5 gives the product specific gravity referred to hydrogen or our specific weight.

Column 6 gives the atomic weight.

Column 7 shows the value of V^v, as represented by n in

$$M\,P + 273\,n \text{ found near } B\,P.$$

Lastly, column 9 gives the determination of V^x which must aid us in selecting our base values, or densities at $B\,P$ in the determinations of the heats of formation.

Being calculated from V^v they must hold the latent heat of vaporization included at that station.

We have, first, seven determinations of the density of iodine, at temperatures ranging from the boiling-point to 1773° absolute centigrade.

These indicate that the rate of mass to volume, when compared with the normal at V^v near $B\,P$ and at 760 mm, after remaining at unity and constant from $B\,P$ to 1273° drops suddenly to 0.66 between this temperature and 1373°, and again, that at 1773° it is reduced to 0.5.

For comparison with this range of results, it can be noted that, with this element, in the various calculations of $H\,F$ which are to follow, these equivalent volumes are 1 to 0.5.

Again, on our chart, bromine varies from 1 to 0.73 while in the $H\,F$ values of Cd Br_2, it is 2 or at the rate of 1 per atom of bromine.

With chlorine, we have two series of experiments, one where the source whence the chlorine is drawn is not stated.

Here, up to a temperature of 1473° abs. C. the volumes held per atom are constant and at unity, while in the second series, where the chlorine is derived from $Pt\,Cl_2$ entirely different results are shown. In this case the density yields the volumes as varying from 0.82 to 0.66.

In our calculations of $H\,F$ we have these values at 1, 1/2 and 1/3 in various combinations.

It is claimed that the variations, in these experimental results, with the matter from divers sources, as given, indicates precisely what it is sought here to prove, namely, that in each combination a special V^x, or a variable rate of mass to volume, is derived from, or caused by, the configuration of the material with which it is about to enter in combination.

Table XXIV shows oxygen, mainly, with one volume per atom, and our calculations do likewise.

At the same time, it is to be noted that on Table XXV one of those showing the calculations of $H\,F$ in detail, some data are presented concerning allotropic changes, though they do not properly belong there.

The one in question is the change of 96 grams of ozone to 96 grams of oxygen, binding 68000 cals.

Seen from our point of view, this change can be measured as follows:

We are naturally obliged to recognize that the unit of energy of cohesion is centered in what we have specified as the half atomic weight. In the perissad element only two of these factors appear, and the full atomic weight ordinarily becomes the acting mass unit.

Among the artiads, however, two, three or more units of cohesion may appear. We find oxygen rated with this variety. In its allotropic form three units are recognized, changing the configuration. Then the mass units for oxygen and ozone should be written: 1st, for O as $\frac{16}{2} \times 2 = 16.$

$$\text{2d, for Oz as } \frac{16}{2} \times 3 = 24.$$

These masses are then just one half of the recognized mole-

cular weights of these bodies at laboratory temperature and 760 mm.

But for our purposes they represent the actual unit mass, in each case, which is subject to a volume of expansion. Thus the mass 16 is that held per unit volume in oxygen at laboratory temperature and at 760 mm, for it represents the atomic weight and its specific gravity (H) at that station.

Then we should be able to show that 24 represents ozone in a similar manner, with the exception that its energy is doubled, for the two volumes of expansion are required to cover that of the full acting mass.

From the determinations of Prof. Dewar we have the weight of one liter oxygen equal to 4.42 grams at $B\ P$ or 90.5 abs. C. and 760 mm. pressure. Then its specific weight equals 49.35.

If we assume the gain in density by the change from station V^{v} to $B\ P$ to be 1.35 times the weight of the hydrogen unit, we have a theoretical specific weight of our material of 48 at $B\ P$.

We can then determine the numbers of expansions submitted to by the common mass, in each of the materials, from this station to the laboratory temperature.

We must, however, bear in mind 1st, that the melting-point or the origin of the gaseous expansion falls at 86.3° abs. C. and that this determination is only approximate, though the difference in degrees is small; 2d, that our chart XXII shows, as regards a second limit, that this density (H) continues to a temperature of about 1840° abs. C.

But under the conditions stated above, we have:

$$\text{For oxygen } \frac{\text{Specific Weight}}{\text{Unit Weight}} \times 1 = \frac{48.}{16.} = 3. = V^{x}$$

$$\text{For ozone } \frac{\text{Specific Weight}}{\text{Unit Weight}} \times 1 = \frac{48}{24}. = 2. = V^{x}$$

Then at laboratory temperature the volumes holding this specific weight become 3 and 2 respectively, and 24 hydrogen units of ozone near that station under 760 mm. pressure represent the energy of two volumes of expansion.

We arrive, in this manner, at a position determined by Soret, who found that ozone was produced when three volumes of oxygen were compressed into two. He thus retained the same acting mass, but compressed it to the conditions specified.

We can now consider our unit of ozone either as determined by its specific weight 48, or by its unit mass 24.

In the latter case, however, we must bear in mind that the body consists of two such units of expansion or that n equals 2.

From this point we can revert to the experimental determination of the heat energy required to change 96 grams of ozone to oxygen. This experiment then covers the difference in the amounts of energy required to expand the same mass, in the one case, to three volumes, and in the other to two volumes.

This latter state is, however, coupled with the condition that each mass unit is 24, while in the earlier it is 16.

Upon this basis we have for ozone in the experiment $\frac{96}{24}\times 2$ expansions $= 8$ volumes, also the expansion of oxygen relatively to the same as $\frac{3}{2}$ or 1.5 that of ozone. Then the expansion of oxygen $= 1.5 \times 8$ vols. $= 12$ volumes.

Our calculations are given in detail upon Table XXV for the milligram molecule, and are based upon the observation that, if ozone is held at 100° C. thereby absorbing energy it slowly changes to oxygen.

This determines our value of t^c as 373° abs. C. and under our methods of estimating the chemical energy as the product of the average stress into the strain of volume, we have, as shown on said sheet,

$$\begin{array}{lll} \text{For O } V^x = 12. & CE = & 173.60 \text{ Calors} \\ \text{" Oz } V^x = 8. & CE = & \underline{103.72} \quad \text{"} \\ & & 69.88 \end{array}$$

$$\text{Then Coef. } B = \frac{68000}{69.88} = 973.1 \text{ or } 97.31\%.$$

It is evident, however, that if the experiment could be confirmed at a slightly lower temperature, the comparison would be more favorable. For while, as represented, the mass per volume alone varies, and the acting stress $\frac{Z^c - Z^z}{2}$ is constant, in both cases, still this value of Z^c would be reduced with the temperature of observation t^c.

The evidence given above tends to show that the allotropic

forms of oxygen and ozone are based upon the numbers volumes of expansion of the various parts carrying the uni of mass as dispensers of energy. We have also a certain amou of evidence as to the nature of the changes we would be oblig to expect if, as is sometimes suggested, all elements were d rived from a common source.

Returning to our records of Chart 1 we find that in the ca of the element sulphur the volumes holding the unit ma varies from 6 to 2, while in the calculations of HF they va from 6 through 2 to 1/4.

With Hg we find five experimental tests, each with V^x eq to one, while this condition occurs in our calculations as well.

There seems, then, to be little doubt that the changes have proposed, in the assumption of V^x for V^v lie within t possible ranges covered by the variations of cohesion wi variable pairs of dissimilar atoms, for they are covered by chan that are known to occur under specific charges of heat energy.

Our formulæ in their final form are:

CE = average stress × volume at temperature of calculati

Here the average stress equals $\frac{Z^c}{2}$ or $\frac{Z^c - Z^z}{2}$ and

$$V^c = V^x\left(1 + \frac{t^c - BP}{273}\right).$$

$$V^x = \frac{\text{Specific Wgt. }(H)}{\text{Atomic Wgt.}} \times V^v.$$

It seems necessary now only to call attention to the reco showing the detail calculations of the heats of formation, as results of these formulæ.

They are shown upon Tables XXV, XXVI and XXVII. each of these the details are recorded as follows:

Column 1 shows the reaction in question.

Column 2 identifies the line on which the data for each reag or for each product, are spread.

Columns 3 and 4 give the respective melting and boi points, in absolute degrees centigrade.

Column 5 gives the temperature of calculation, or the v of t^c.

Column 6 shows the value of the final term $-a$, in the form of stress. By substituting any value of X in $X + 26.24\,Z - a$ the corresponding value of Z may be calculated.

...als. Coef. B Theoretica

V^x	V^c
1	1.326
1	4.3179
2	2.
1	1.
2	4.8654
1	1.1941
1	1.
2	3.2806
1	1.
1	1.
0.5	2.7945
1	2.7765
1	1.
	0.59707
	0.5787
	0.8837
	0.25
	0.7095
12	13

cals.

$$\text{Coef. } B = \frac{H\ F \text{ cals.}}{\text{Summa } CE \text{ Calors}}$$

Theoretical value of Coef. $B = 1000$

V^x	V^c	Summa CE Calors	$H\ F$ cals	Coef. B
1	1.326	18.805	93244	93244
1	4.3179	94205		=
				92.995
		113010		
2	2.	20.015		1003.
		92.995		
1	1.	11.227	63160	63160
2	4.8654	58.178		=
				63.507
		69.405		
1	1.1941	5.898		994.5
		63.507		
1	1.	11.292	34.310	34.310
2	3.2806	27.456		=
				33.009
		38.748		
1	1.	5.739		1030.
		33.009		
1	1.	24.813	39800	39800
0.5	2.7945	80.79		=
				39.195
		105.603		
1	2.7765	66.408		1015.4
		39.195		
1	1.	5.308	5830	5830
½	0.59707	5.191		=
				5.7962
		10.2301		
½	0.5787	4.4339		1005.8
		5.7962		
½	0.8837	12.000	4740.	4740
½	0.25	2.473		=
				4.8837
		14.473		
½	0.7095	9.6396		980.5
		4.8337		
12	13	14	15	16

Column 7 gives the values of Z^c as determined for the different situations. The minus signs have been omitted, as all determinations are for the gaseous condition.

Column 8 shows the average stress $Z^c/2$.

Column 9 gives Z^z, the actual stress to be found at absolute zero, in those cases where Z is still negative at that point.

Column 10 shows the average increase of stress between absolute zero and t^c. It is indicated as a value of $\frac{Z^c - Z^z}{2}$.

Column 11 shows those values of V^v which can be determined from $B\ P$.

Column 12 gives the values of V^x, indicating the volume in its relation to the unit mass, that expresses in the reaction the density at the time of contact.

Column 13 gives the expanded volume at V^c, or the volume holding the prescribed mass at that temperature, and the one in which the stress has reached its final value.

Column 14 shows the product of stress and V^c, as values of $C\ E$. Here, first, those of the reagents are added, and later that of the product deducted. The remainder we designate as the "Summa $C\ E$ (Calors)." It expresses the energy the heats of formation.

Column 15 shows the values in calories of the experimental determinations of $H\ F$ by Julius Thomsen.

The former are the $\frac{1}{1000}$th part of the latter. Then the Coef. $B. = \frac{H\ F \text{ cals.}}{\text{Summa } C\ E \text{ (Calors)}}$ by its approach to this theoretical value, expresses how closely the calculated value agrees with the experimental.

It should be noted that, while some fall above 1000, others fall below. The average of the nineteen coefficients, however, is 997.53 or 99.73%.

At this point it may be an advantage to offer an example of these calculations following the methods as described.

It will be recalled that on page 127 the different stresses in the reaction N_2O were calculated.

In this case t^c fell at laboratory temperature and $\frac{Z^c - Z^z}{2}$ was determined for both reagents and product as 5.582 Kgms.

per square millimeter. The method described at that point will suffice to show how any stress can be calculated, though that shown is a special adaptation.

Under the methods described the relative volumes V^x are chosen, as follows:

For N_2,	$V^x = 2.$
" O,	$V^x = 1.$
" N_2O,	$V^x = 6.$

Secondly, when expanded to V^c under $V^c = V^x \left(1 + \frac{t^c - B\,P}{273}\right)$ these volumes become respectively:

For N_2,	3.5174
" O,	1.742
" N_2O,	8.37

Then the total heat energy measuring their respective conditions of cohesive energy, under atmospheric pressure and at 293° abs. C. can be calculated as the product of stress into the strain of volume, and can be summed as follows:

N_2	5.582×3.5714	$= 19.9294$	Calors.
O	5.582×1.742	$= 9.7235$	"
		29.6529	"

Rebound in the product, we have:

N_2O $\quad 5.582 \times 8.37 = 46.714$

Summa $C\,E$ (Calors) $= -17.062$ "

Experimental determination of $H\,F$ equals $-$ 17470 cals.

$$\text{Hence Coef. } B = \frac{-17470}{-17.062} = 1024 \text{ or } 102.4\%.$$

In closing, it is only necessary to recall that this stress, developed by heat against cohesion, is possibly the osmotic pressure. If so, it is, without doubt, a resultant originating with a motion which increases directly as the temperature absolute centigrade.

As the volume increases in matter, with rising temperature the energy of cohesion is measured by the changes we have endeavored to develop.